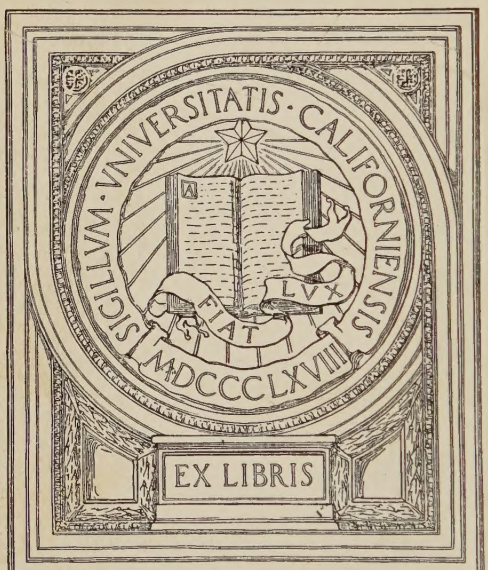

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PHYSICAL CHEMISTRY FOR COLLEGES

A COURSE OF INSTRUCTION BASED UPON THE FUNDAMENTAL LAWS OF CHEMISTRY

BY

E. B. MILLARD

Associate Professor of Physical Chemistry, Massachusetts Institute of Technology

SECOND EDITION

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PREFACE TO SECOND EDITION

In preparing this second edition no fundamental changes have been made in the plan of presentation, but certain topics have been brought up to date or presented more fully as their importance has increased during the past years.

A few paragraphs on thermodynamics have been introduced to stimulate the curiosity of the exceptional student. This material has usually been placed in the footnotes so that it will not interfere with the student who seeks only a casual acquaintance with physical chemistry. In adding this material no attempt has been made to produce a "thermodynamic" textbook, especially as this has recently been admirably done.

The chapter on X-rays and crystal structure has been considerably enlarged. New work on ionized solutes has necessitated rewriting the chapter on conductance and transference. It has seemed best to present the facts and theories separately in this connection. In the chapter on thermochemistry the sign of the heat of reaction has been changed to conform with thermodynamic usage, that is, heat is considered positive when it is absorbed by a reaction.

The plan of arranging problems at random at the end of each chapter has been retained in order that the student may be required to select the laws which he applies to the solution of these exercises.

The author is indebted to those who have called attention to errors and omissions in the first edition. Whenever suggestions have been received which do not represent a difference in point of view, he has attempted to meet these suggestions in preparing the new edition. It is a pleasure to acknowledge in this place the benefit which has been derived from the suggestions of those using the text. Criticism of the material as now presented will be gratefully received and carefully considered. It will be deemed a favor if those who find errors in the text will call the attention of the author to them.

E. B. Millard.

Massachusetts Institute of Technology,
Cambridge, Mass., *April*, 1926.

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PREFACE TO FIRST EDITION

This book has been prepared to bring before college students certain of the more important aspects of physical chemistry, together with accurate modern data which illustrate the applicability of its laws to the phenomena observed in the laboratory. It has been assumed that the student is familiar with inorganic and analytical chemistry, that he has had an adequate course in college physics, and that the simple processes of calculus are familiar to him.

No attempt has been made to cover the whole of physical chemistry in a single volume; its most important topics have been treated at such length as the size of the volume allows, and numerous references to recent periodical literature are included for those who would pursue any given topic further.

The limitations of the orthodox laws of physical chemistry have been emphasized more than is commonly done in beginning courses of physical chemistry. To this end the illustrative data have been carefully chosen from modern experimental work, in order to minimize the "experimental errors" which are so often used to conceal real deviations of a law from the facts it is intended to express. A trusting belief in inadequate physical laws will only retard the scientific progress of a student, and weaken his faith in adequate laws; whereas a wholesome appreciation that physical chemistry is an unfinished and growing science may stimulate thoughtfulness and research. The proper time to encourage a research attitude is in the very beginning of a student's chemical career.

A qualitative treatment of the subject, so-called descriptive physical chemistry, may be obtained from the text alone; but careful consideration and study of the numerous tables of data will be required if anything approaching an appreciation of quantitative physical chemistry is desired. A quantitative point of view has been maintained as far as possible, even in the descriptive material.

Rather more tabulated data have been presented than might seem necessary in a beginning text. This is done to furnish the

basis for numerous problems of a quantitative character. Many such problems should be solved in the course of a term, since they stimulate interest and increase the usefulness of the material taught in the class room. The problems at the end of each chapter will not be sufficient to test the ability of general classes; they are type problems in many instances, and should be supplemented by others designed by the teacher to suit the needs and ability of his particular class. Problems should often be assigned for which data must be obtained directly from tables in the text. Much of the value of problem working is lost when a student knows he must use all of the data given him and no other; this too often results in suggesting the entire solution of the problem. Moreover, fresh problems must be given every year if fresh interest in physical chemistry is maintained; this can be done only when ample data are at hand. Some of the more difficult problems at the end of a chapter should be worked by the instructor in class.

References to original sources are not intended primarily as citations of authority for statements made; they are first of all suggestions for further reading. With this in mind, most of the references are to periodicals in English, and to those which are available in small libraries. The author has not hesitated to draw upon little known periodicals when the material to be obtained in them suited the needs of the text; he has not ignored foreign publications in the search for material; but for obvious reasons much of the best data is published in the widely circulated journals, and to these most of the reference work is confined.

The author is greatly indebted to Prof. James F. Norris and to Mr. Charles R. Park for reading the manuscript and making many helpful suggestions and criticisms based on their teaching experience. Their assistance has aided materially in detecting errors. He is also indebted to many other friends for kindly interest and encouragement during the preparation of the manuscript. It will be considered a favor if those who find errors of any kind in the text will communicate them to the author.

E. B. Millard.

Massachusetts Institute of Technology,
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PHYSICAL CHEMISTRY FOR COLLEGES

CHAPTER I

INTRODUCTION. DETERMINATION OF ATOMIC WEIGHTS

Physical Chemistry treats of the applications of fundamental physical laws and theories to the phenomena of chemistry. A proper understanding of these laws and their applications enables us to predict, for example, the conditions under which certain chemical substances are at equilibrium, or the extent and velocity of reactions which take place between them. The usefulness of these calculations will be apparent from the many applications cited in the following pages.

Laws of Nature. (Results of Experience).—Some of the general laws relating to chemistry appear to be absolutely exact; they describe faithfully the results of most carefully conducted experiments; apparent deviations of these laws become less and less as the manipulative skill employed in testing them increases. Among these laws may be mentioned the law of the indestructibility of matter (conservation of matter), the law of definite proportions, and Faraday's law of electrolysis. Other so-called laws fail to describe actual conditions, and the deviations, which are not due to experimental errors, are of considerable magnitude. These laws are approximations which show in a qualitative way the behavior of substances, and which more or less accurately describe their quantitative relations. Thus no law is known which expresses exactly the change of pressure of a gas as the volume or temperature is decreased, but approximations are known which show these changes to within about 1 per cent or less for moderate variations of volume or temperature.

We shall compare each law with the results of experiment and aim to form an opinion as to whether judgment is required in the use of a "law," or whether it is rigidly accurate under all conditions. Some approximate laws describe the results of experiment quite accurately under certain conditions, but deviate to a larger extent under other conditions. When this is the case, the limiting conditions under which the law is accurate to within 1 or 2 per cent will be stated.

The statements put forward as laws of nature are sometimes the result of experience alone (empirical laws). There is in these cases a possibility that some future experience will demonstrate the untruth of what we have considered as a law, but the probability of this becomes less and less as the number of experiments increases. No change has ever been observed in the total mass of the substances involved in a chemical reaction; that is, no matter has ever been destroyed in changing it into other forms. As the methods of experiment have become more and more refined, and as the experimenters have become more skilful in their work, this law remains unshaken as a statement of universal experience, and it is now commonly accepted as an exact law of nature. But it has never been demonstrated that such a change of mass, or a destruction of matter, is absolutely impossible. Other simple laws, such as Boyle's law for gases, are also the result of experience, but as the experimental methods have become more refined, real deviations of these laws from the facts observed have been discovered. These experiences point to a failure of the supposed laws to explain completely the behavior of substances, and are not to be traced to errors of experiment.

Proper reserve should always be exercised in drawing general conclusions from a set of experimental data. The phenomena of nature are often more complex than we think, and what appears to be a general law is often true only under restricted conditions. A statement of such a law without at the same time mentioning the conditions under which it is true is, therefore, a misrepresentation of the facts.

Laws of Thermodynamics.—Under this heading we may state for future reference two laws of the greatest importance which may be used in a surprisingly wide variety of ways. One of them

is probably familiar under another name. **First Law:** When energy is converted from one form into another, no loss in total energy takes place. This might also be stated: The total energy content of the universe is a constant. The **Second Law** may be conveniently stated in two parts: Work may not be produced by a reversible cycle of changes operating in surroundings of constant temperature. When work is produced by a reversible cycle operating between two absolute temperatures T_2 and T_1, the quantity of work performed by the cycle is

$$w = \frac{q(T_2 - T_1)}{T_2},$$

where q is the heat absorbed at the higher temperature T_2. The full power and meaning of these laws is only to be obtained from long acquaintance and use. These laws may be stated in a variety of other ways.[1] It will be observed that the second one is a limitation upon the first; for, while work may be quantitatively changed into heat, the reverse change is subject to further restrictions in addition to that required by the first law. Several applications of each one will be given in the following chapters.

Theories are plausible beliefs advanced to explain observed facts. They serve to guide further experiments in a given field, but are often incapable of direct proof. Thus the theory that a gas consists of molecules, separated from one another by considerable distances and in rapid motion, offers a ready explanation of the compressibility of gases, of their diffusion, of their ability to mix with other gases in all proportions, and of practically all their properties, but the theory is not capable of direct proof. That is, no one has been able to see or experiment with a single gaseous molecule. The evidence in favor of the truth of the theory is, however, abundant and convincing; no facts are known which contradict it; and deductions based on this theory are in accord with the results of experiment. It is therefore universally accepted as a fact, but is referred to as the kinetic *theory* of gases.

Many such theories are found in chemistry. They are accepted so long as they are in accord with the facts; they may be altered to fit new discoveries, but they should be discarded in

[1] An excellent discussion of these laws is given in Lewis and Randall's "Thermodynamics," to which reference should be made for many applications of them to the problems in physical chemistry.

favor of newer and more satisfactory ones when they seriously conflict with the results of experiments.

Indestructibility of Matter.—It is a familiar fact that matter can be changed into various forms by combination and rearrangement of the elements in various ways without any loss in the total mass of material. In other words, the total mass of all the substances taking part in a chemical reaction is unchanged by the reaction. The many operations of analytical chemistry depend on the validity of this fact; but since there is no reason why there *might* not be a change of mass during chemical change, it has been necessary to test this belief experimentally before accepting it as a fact. Perhaps the best known tests of this character are Landolt's experiments[1] extending over a period of 20 years, and devoted to a careful study of 15 different chemical reactions, which were examined with great skill and patience. The reacting substances were enclosed in the separate arms of sealed vessels, such as that of Fig. 1, to prevent the possibility of mechanical loss of material. The tubes were weighed on a very sensitive balance, using a counterpoise of the same size and shape. Then by tipping the vessel, the two solutions were brought in contact a little at a time, so that the heat effect of the reaction would not expand the bulb and thus cause an apparent change in weight by increasing its air displacement. After the reaction had been completed the vessel was weighed again. The weighings were made several times, and an average taken. As a result of his work, Landolt concluded that if there was a change in mass during chemical reaction, it was less than the error of weighing, which was one part in about 10,000,000.

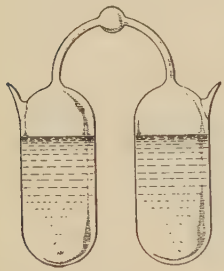

Fig. 1.

The later work of Manley[2] on the reaction $6AgNO_3 + 6FeSO_4 = 6Ag + 2Fe_2(SO_4)_3 + Fe_2(NO_3)_6$ was carried out with exceeding care. Two tubes of the form shown in the figure were filled with silver nitrate solution in one limb and ferrous sulfate solution in the other, and their weights were made as nearly equal as

[1] *Z. physik. Chem.*, **12,** 1 (1893); *Sitzb. preuss. Akad. Wiss.*, **1908,** 354.

[2] *Phil. Trans. Roy. Soc. London,* (*A*) **212,** 227 (1913).

possible by the addition of small quantities of water, after which the tubes were sealed shut and hung on the arms of a very sensitive balance. After a series of careful weighings extending over a period of several days, it was determined that the difference in weight of the two tubes was 0.026 mg. in one experiment. The contents of one tube were mixed, causing the reaction given above to take place, and after a time the difference in weight was again determined. Now if there is a change in mass during chemical reaction, the difference in weight between the two tubes should change, as a reaction has taken place in one of them and not in the other. After the reaction the difference in weight between the two tubes was found to be 0.022 mg., which corresponds to a change of 0.004 mg. Since the total weight of reacting substance was about 127 grams, the change in weight was one part in 32,000,000, which is again less than the probable error of the weighing. In another series of experiments the reaction between barium chloride and sodium sulfate was examined with the same care, and it was shown that any change in weight must be less than one part in 100,000,000.

In making these weighings the balance was carefully maintained at a constant temperature and shielded from air currents; the tubes were handled by a system of levers so as to protect the balance from heat from the body of the operator; and a period of some days elapsed between the chemical reaction and the final set of weighings. During this time the tube was kept under a bell jar and otherwise protected from dust or contamination of any kind.

In the light of these experiments there is no room for doubt as to the exactness of the law of indestructibility of matter. We may therefore state as an *exact* law of nature that matter (anything which has mass) does not change in mass during combination or chemical decomposition.

Elements and Compounds.—The number of kinds of matter is very great indeed, but attempts to resolve matter into its ultimate constituents have brought to light about 92 substances which cannot be decomposed into simpler substances. These are called elements. The number of experiments performed upon most of the known elements is so great as to make it improbable

that they consist of two substances which may be separated later by some chemical process.[1]

There are a few more elements yet to be discovered, but the periodic arrangement of the elements makes it probable that the number of undiscovered elements is small. Thus, the discovery of an element similar to manganese and of higher atomic weight would not disturb the periodic arrangement, for in the periodic table it was necessary to leave a blank corresponding to such an element. But the discovery of an alkali element with an atomic weight between sodium and potassium would give us an element for which there was no place in the periodic table, and thus disturb this arrangement. Hence, the existence of such an element is improbable. All of the known kinds of matter consist of combinations of these elements in various proportions. Practically all kinds of matter have been decomposed into their elements, or into simple compounds which may be so decomposed, and a vast number of the substances in nature have been built up from the elementary substances in the laboratory. In addition, many substances not found in nature have been so made. Certain substances, notably the complex compounds occurring in plants and animals, have not so far been prepared synthetically.

Law of Definite Proportions.—This law states that the quantity of an element which will combine with a given weight of another element to form a pure chemical compound is a fixed quantity, regardless of the method of preparation of the compound. In other words, the percentage of each element in a pure compound is always the same, and the presence of an excess of one element does not result in the formation of a compound containing more of it.

Table 1 shows data[2] on the synthesis of silver bromide from carefully purified silver and bromine, together with the weight of bromine combined with each gram of silver. Elaborate precautions were taken to assure the purity of the substances weighed, and to avoid mechanical loss during the synthesis.

[1] The question of isotopes is discussed in Chapter XIII.

[2] Baxter, *J. Amer. Chem. Soc.*, **28**, 1322 (1906).

TABLE 1

Weight of silver	Weight of silver bromide formed	Grams of bromine combined with each gram of silver
5.01725	8.73393	0.74078
5.96818	10.38932	0.74079
5.62992	9.80039	0.74077
8.13612	14.16334	0.74080
5.07238	8.82997	0.74079
4.80711	8.36827	0.74081
5.86115	10.20299	0.74078
6.38180	11.10930	0.74078
6.23696	10.85722	0.74079
9.18778	15.99392	0.74078
8.01261	13.94826	0.74079
8.59260	14.95797	0.74079
8.97307	15.62022	0.74079
		Average 0.74078

The synthesis was conducted by supplying ammonium bromide to a weighed quantity of silver which had been converted into nitrate, until no more bromine would combine with the silver, after which the silver bromide was collected and weighed.

Another example of the law of definite proportions is shown in Table 2. A quantity of iron was converted into ferric oxide and heated with an excess of oxygen until no more would combine with it.[1] The ferric oxide was weighed, then heated in a current of hydrogen until all of the oxide had been completely reduced to iron, which was then weighed.

TABLE 2

Weight of iron	Weight Fe_2O_3	Per cent Fe in Fe_2O_3
2.78115	3.97557	69.956
3.42558	4.89655	69.959
3.04990	4.35955	69.959
4.99533	7.14115	69.951
4.49130	6.42021	69.956

[1] RICHARDS and BAXTER, *Proc. Am. Acad. Sci.*, **35**, 253 (1900).

The synthesis of tin tetrabromide is shown in Table 3. It will be seen again that the composition of the product is constant,[1] in so far as it is possible for the best quantitative chemistry to determine it.

TABLE 3

Weight of tin	Weight of $SnBr_4$ formed	Per cent tin in $SnBr_4$
2.8445	10.4914	27.113
4.5735	16.8620	27.123
4.5236	16.6752	27.119
3.0125	11.1086	27.116
2.8840	10.6356	27.113
3.0060	11.0871	27.123

Molecular Theory.—The theory that matter of all kinds consists of very small particles or molecules is now commonly accepted as a fact. This theory is in complete accord with all the known facts of chemistry; it explains in a simple way all of our chemical reactions; and it forms the basis of modern chemical thinking. The molecules of which a substance consists cannot be divided into smaller particles without a complete change in the properties of the resulting particles. They are the limit of divisibility for a given kind of matter. When all of the molecules in a mass of matter are exactly alike, this mass of matter is called a *pure substance*. When there are two or more kinds of molecules present the mass of matter is called a *mixture*. A pure substance may be prepared from one containing other kinds of substances by treating it with a solvent which will dissolve one substance and not the others, by distilling it if the undesirable substances are not volatile, by treating it with a reagent which will convert the undesirable matter into an insoluble form or a volatile form, by crystallizing it several times from some solvent, etc. It is probably true that we are unable to prepare substances of such purity that they contain only one kind of molecule, but when the other molecules have been so far eliminated that their effect is not detectable by our most sensitive means, we call the resulting product a pure substance.

[1] BONGART and CLASSEN, *Ber.*, **21**, 2900 (1888).

If all of the molecules of a pure substance are exactly alike, each of them must contain the same percentage of each constituent element as the whole mass of substance. It is certain that all of the molecules must be exactly alike in every respect, for otherwise, by availing ourselves of the properties in which they differ, we could effect a separation into two portions having different properties, that is, into two pure substances. Hence every molecule must have the same composition as the whole mass of pure substance. Two matters at once claim interest: the relative weights of the molecules of different substances, and the way in which the molecules are formed from their constituent elements.

The relative molecular weights cannot be determined from comparisons of single molecules, on account of their small size. But equally satisfactory results may be obtained if we have a way of counting out the same number of molecules of each substance for comparison. Avogadro's law furnishes such a method.

Avogadro's Law.—This law states that equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules. As this law is discussed in some detail in the next chapter, we will not take up here the line of thought on which it is based or the proof of its validity. In order to determine the relative weights of the molecules of two substances, we need only compare the weights of equal volumes of them in the gaseous state under similar conditions, since we are then comparing equal numbers of molecules. Naturally, the next step is to adopt some substance as a standard of reference for relative molecular weights, and chemists now by common consent have adopted 32 as the "molecular weight" of oxygen. Since they employ the gram as a unit of weight, 32 grams of oxygen is therefore accepted as a "gram-molecular weight," or a gram-molecule. On account of the extensive use of this term, it has been abbreviated to "mol," which is written without a period. It is not an abbreviation of the word "molecule," but a separate new word meaning gram-molecular weight.

A **molecular weight** of a gas is that weight of it which occupies, under any conditions of temperature and pressure, the same volume as a molecular weight (32 grams) of oxygen under these same conditions. "Standard" conditions are a temperature of

0° and a pressure of 1 atmosphere, but it should be made clear that comparisons are not restricted to these experimental conditions. A **molecular volume** of a gas is the volume of 32 grams of oxygen. Then *the molecular weight of a gaseous substance is that weight of it which occupies a molecular volume.* We may, of course, determine the molecular volume under any convenient conditions from the volume of 32 grams of oxygen, and compute the weight of a molecular volume from the weight of any known volume. Experimental procedures for this are described in the next chapter.

The choice of 32 as the molecular weight of oxygen is in conformity with 16 as its atomic weight. The following reasoning will show that the two numbers are not separate standards.

One volume of oxygen and two volumes of hydrogen combine to give two volumes of water vapor. Avogadro's law, therefore, requires that the number of molecules of water vapor formed be equal to the number of hydrogen molecules used, and that it be twice the number of oxygen molecules used. But each molecule of water must contain a whole atom of oxygen, since the atoms are indivisible, and it follows that the oxygen molecules contain two atoms each. In conformity with our choice of 32 for the molecular weight of oxygen, which often forms compounds containing only a single atom per molecule, it will be necessary to take 16 as its atomic weight. Thus 32 grams of oxygen will contain the same number of molecules as 16 grams of oxygen contains atoms.

Atomic Weights.—Mention has been made of the fact that molecules of compound substances contain more than one kind of element. A molecule is, therefore, not the smallest division of matter, though it is the smallest one capable of separate existence. The parts of molecules are called atoms, and molecules are made of a whole number of atoms, since these are defined as the smallest particles of matter. When a pure substance is an elementary one, all of the atoms in its molecules are exactly alike. The number of atoms in a molecule of one element may be one (as in helium and argon, the vapors of metals, and other substances at very high temperatures), two (in most of the common elementary gases), or more, but the atoms are all exactly alike, since, when these elements react with another elementary substance, only

one kind of product is formed. When the molecule (the particle capable of separate existence) contains only a single atom, the atomic weight is identical with the molecular weight. If an elementary molecule contains two atoms, its atomic weight is half of its molecular weight. Thus the molecular weight of hydrogen is two, and its atomic weight is one; just as the choice of 32 as the molecular weight of oxygen made necessary 16 as its atomic weight.

An atomic weight of an element is the smallest weight of it found in a gram-molecular weight of any of its compounds. A molecule must contain a whole number of atoms of any element; a gram-molecular weight of a compound contains a whole number of atomic weights of each element in it. Thus the accepted values of atomic weights represent the smallest quantity of each element found in a gram-molecule of any compound so far; and the possibility of discovering a compound with less of the element per molecular weight always exists. The probability of this discovery becomes less as the number of compounds studied increases. There are other ways in which the value of an atomic weight may be checked, such as its specific heat, its place in the periodic system, and the relation between its compounds and other similar compounds. The atomic weights given in the table on page 17 are probably the true ones in every case.

Atomic Weight Methods. (*a*) *From Gas Densities Alone.*— Where the number of atoms in a molecule of an elementary substance has been established from the volumes of the gaseous substances formed by it upon reaction with other gases, the atomic weight may be determined by dividing the molecular weight by the proper whole number. Similarly, the atomic weight of bromine may be determined by subtracting from the molecular weight of hydrogen bromide the atomic weight of hydrogen, since its molecule is known from combining volumes to contain one atom of each element. But Avogadro's law is one which becomes more exact as the gases under comparison are studied at lower pressures. On the other hand, the difficulty of determining the weight of a volume of gas increases as the pressure is reduced, since the quantity of substance weighed becomes smaller in comparison to the weight of the vessel in which it is contained. Skilful work will overcome the last-mentioned diffi-

culty, but from the deviations of Avogadro's law at higher pressures there is no escape. The problem of determining exact gas densities at pressures for which Avogadro's law is also exact has been solved by the careful experiments of Guye and his students. Their work on methyl fluoride[1] may serve as an illustration of the method, and of the results obtained. The weight of a liter of gas at 0° was determined for pressures of 1 atmosphere, two-thirds of an atmosphere, and one-third of an atmosphere; and from these figures a value of d/p, the ratio of density to pressure, at 0° was calculated for each pressure. These values represent the weight which a liter of methyl fluoride would have at 1 atmosphere if the deviation of Avogadro's law were as small as they are at the pressure of the determination. The data are shown in Table 4.

The deviations become smaller at still lower pressures, but the quantity of gas to be weighed is too small for accurate work.

These values of d/p may be plotted against the pressure as is done in Fig. 2, and (since the points fall on a straight line) the curve extended until it cuts the axis of zero pressure. This gives the "limiting density" or the weight of a liter of the substance

Table 4

Pressure (atmospheres)	Weight of a liter of methyl fluoride at 0° (grams)	Ratio d/p
1.0000	1.5454	1.5454
0.6667	1.0241	1.5361
0.3333	0.5091	1.5274

if it behaved as an ideal gas. As will be seen from Fig. 2, this value is 1.5177. Since the volume of a mol of ideal gas under standard conditions is 22.410 liters, the exact molecular weight of methyl fluoride is 22.410×1.5177, or 34.012. The formula is CH_3F, and the atomic weights of carbon and hydrogen are accurately known, namely, 12.00 and 1.008, respectively. Thus

[1] Moles and Batuecas, *J. chim. phys.*, **17**, 537 (1919).

$12.00 + 3 \times 1.008 + F = 34.012$, from which the atomic weight of fluorine is 18.99.

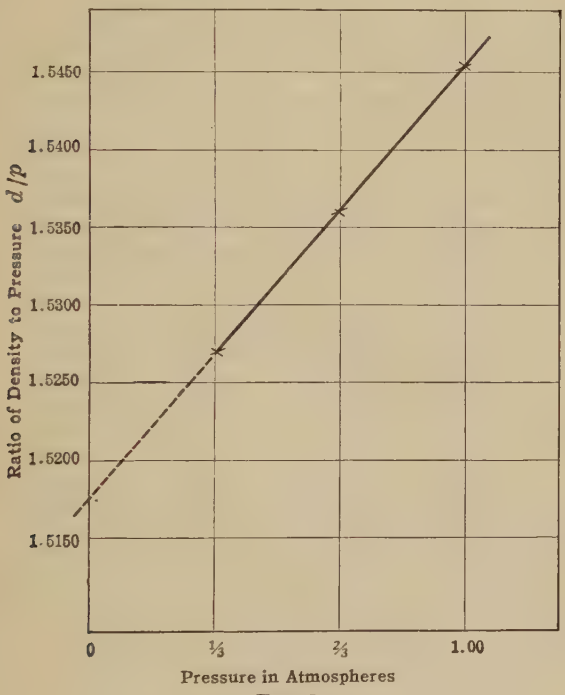

FIG. 2.

(*b*) *From Molecular Weights and Compositions by Weight.*— A molecular weight of a compound must contain a whole number of atomic weights of each element in it. When large numbers of gaseous compounds of any element are examined, the smallest weight of an element found in a mol of any of its compounds is called the atomic weight of that element. Since determinations of molecular weight are not usually performed with great accuracy, careful analytical data are used to supplement this work. An example will make this point clearer. In the following table are given some approximate data for gaseous nitrogen compounds, using only whole numbers.

TABLE 5

Substance	Weight of a molal volume of gas	Per cent nitrogen in the compound	Weight of nitrogen in a mol of gas
Nitric oxide	30	47	14
Ammonia	17	82	14
Nitrous oxide	44	64	28
Nitric acid	63	22	14
Nitrosyl chloride	66	21	14
Hydrazine	32	87	28

It is seen from this table that no nitrogen compound contains less than 14 grams of nitrogen per molecular weight; this is, then, the approximate atomic weight. But it is not an *exact* value, since it is based on rough data. An accurate value may, however, be obtained from a quantitative analysis of nitrosyl chloride, since exactly one atomic weight of nitrogen combines with exactly 16 grams of oxygen and one atomic weight of chlorine. The analyses[1] in Table 6 show the composition of nitrosyl chloride. From the average of these figures may be obtained the ratio $N : O = x : 16.000$, leading to an exact atomic weight of nitrogen, namely, 14.001, based on the known atomic weight for oxygen.

TABLE 6

Weight of NOCl	Weight of chlorine	Weight of oxygen	Weight of nitrogen	Loss
0.5341	0.2893	0.1305	0.1142	0.0001
0.4284	0.2319	0.1046	0.0916	0.0003
0.7995	0.4331	0.1954	0.1710	0.0000
0.5121	0.2773	0.1251	0.1095	0.0002

(*c*) *From Analytical Data and Specific Heats.*—The metals and some other elements do not form gaseous compounds at temperatures suited to accurate work, and determinations of their atomic weights must, therefore, rest on other considerations.

[1] GUYE and FLUSS, *J. chim. phys.*, **6**, 732 (1908).

But the weight of a metal which combines with 16 grams of oxygen is either an atomic weight, two atomic weights, half an atomic weight, or two-thirds or three-fourths or two-fifths of an atomic weight, depending on whether the formula of the oxide is EO, E_2O, EO_2, E_2O_3, E_3O_4, or E_2O_5. Analysis of the oxide will give, therefore, an exact value of the atomic weight, or a simple fraction of it, and it requires only a rough determination in some other way to indicate which multiple of the weight combined with 16 grams of oxygen is the true atomic weight. The **law of Dulong and Petit** furnishes such a method of fixing the multiple for metals and the heavy elements. This law states that the atomic heat capacity of solid elements is about 6.2, that is, that the quantity of heat required to raise an atomic weight of an element through a degree is the same for all solid elements. The heat capacity of a gram multiplied by the atomic weight is, therefore, 6.2, or the atomic weight is 6.2 divided by the heat capacity of a gram of element. From the data of Table 2 we see that iron oxide is 69.956 per cent iron; hence the weight of iron combined with 16 grams of oxygen is $x : 16 = 69.956 : (100.00 - 69.956)$, or $x = 37.256$. This is either the atomic weight of iron or a simple fraction of it. The specific heat of iron is 0.115, and 6.2 divided by 0.115 is 54, which is approximately the true atomic weight. It will be seen that 37.256 is about two-thirds of 54, whence the true atomic weight is 1.5×37.256, or 55.88.

The atomic weight of bromine has been established by methods (*a*) and (*b*) at 79.92. From this we may compute the atomic weight of silver from the data of Table 1, since an atomic weight of silver combines with a whole number of atomic weights of bromine. Thus $Ag : Br = 1.000 : 0.74078 = x : 79.92$, whence $x = 107.88$. The specific heat of silver is 0.056, and 6.2/0.056 is 110. Thus the true atomic weight of silver is 107.88.

An example of a more complete set of experiments is the following one, which serves to determine the atomic weights of silver, chlorine, and lithium with reference to oxygen. By reducing lithium perchlorate to chloride it was found[1] that 100 grams of the former gave 39.845 grams of the latter. The formula of the perchlorate is $LiClO_4$, whence it follows that the molecular

[1] Richards and Willard, *J. Am. Chem. Soc.*, **32,** 4 (1914).

weight of lithium chloride is $x : (x + 4 \times 16.00) = 39.845 : 100.000$, or $x = 42.393$. The lithium chloride was then treated with silver nitrate solution made from a weighed quantity of silver, from which it was found that each gram of lithium chloride required 2.54460 grams of silver, giving the atomic weight of silver as 2.54460 times the molecular weight of lithium chloride, or 107.871. This will be seen to be in accord with its atomic weight calculated above from the synthesis of silver bromide. Then, by weighing the silver chloride formed, the ratio of silver to silver chloride was found to be 1 : 1.3287, from which the atomic weight of chlorine is given by $107.871 : (107.871 + y) = 1.000 : 1.3287$, or $y = 35.454$. Returning now to the ratio of lithium chloride to perchlorate, we see that the atomic weight of lithium may be calculated from the atomic weight of chlorine just found. $LiClO_4 : LiCl = z + 35.454 + 4 \times 16.000 : z + 35.454$, or as $100.000 : 39.845$, whence $z = 6.939$.

The atomic weight table published each year is based on all of the determinations made by various methods, the weight assigned to each determination in computing the value for a given element being determined by the number of experiments in a series and the probable error of the average value. These calculations are made by an International Committee on Chemical Elements appointed by the International Union of Pure and Applied Chemistry. The atomic weight of an element is changed when new experiments show that the accepted value is in error, in the opinion of the members of the International Committee. All of the figures stated are significant. Thus 14.008 for nitrogen indicates that this atomic weight is accurate to a thousandth of a unit; 197.2 for gold indicates that the second decimal place is still uncertain. Table 7 gives the atomic weights for use in 1925.

A summary of all the atomic weight work done prior to 1910 is given in the *Smithsonian Miscellaneous Collections*, Vol. 54, No. 3. New work done each year is summarized in connection with the report of the International Committee on Chemical Elements, which is published annually in the leading chemical journals.

TABLE 7.—INTERNATIONAL TABLE OF ATOMIC WEIGHTS FOR 1925[1]

	Symbol	Atomic number	Atomic weight		Symbol	Atomic number	Atomic weight
Aluminum	Al	13	26.97	Molybdenum	Mo	42	96.0
Antimony	Sb	51	121.77	Neodymium	Nd	60	144.27
Argon	A	18	39.91	Neon	Ne	10	20.2
Arsenic	As	33	74.96	Nickel	Ni	28	58.69
Barium	Ba	56	137.37	Nitrogen	N	7	14.008
Beryllium	Be	4	9.02	Osmium	Os	76	190.8
Bismuth	Bi	83	209.00	Oxygen	O	8	16.000
Boron	B	5	10.82	Palladium	Pd	46	106.7
Bromine	Br	35	79.916	Phosphorus	P	15	31.027
Cadmium	Cd	48	112.41	Platinum	Pt	78	195.23
Calcium	Ca	20	40.07	Potassium	K	19	39.096
Carbon	C	6	12.000	Praseodymium	Pr	59	140.92
Cerium	Ce	58	140.25	Radium	Ra	88	225.95
Cæsium	Cs	55	132.81	Radon	Rn	86	222
Chlorine	Cl	17	35.457	Rhodium	Rh	45	102.91
Chromium	Cr	24	52.01	Rubidium	Rb	37	85.44
Cobalt	Co	27	58.94	Ruthenium	Ru	44	101.7
Columbium	Cb	41	93.1	Samarium	Sm	62	150.43
Copper	Cu	29	63.57	Scandium	Sc	21	45.10
Dysprosium	Dy	66	162.52	Selenium	Se	34	79.2
Erbium	Er	68	167.7	Silicon	Si	14	28.06
Europium	Eu	63	152.0	Silver	Ag	47	107.880
Fluorine	F	9	19.00	Sodium	Na	11	22.997
Gadolinium	Gd	64	157.26	Strontium	Sr	38	87.63
Gallium	Ga	31	69.72	Sulfur	S	16	32.064
Germanium	Ge	32	72.60	Tantalum	Ta	73	181.5
Gold	Au	79	197.2	Tellurium	Te	52	127.5
Helium	He	2	4.00	Terbium	Tb	65	159.2
Holmium	Ho	67	163.4	Thallium	Tl	81	204.39
Hydrogen	H	1	1.008	Thorium	Th	90	232.15
Indium	In	49	114.8	Thulium	Tm	69	169.4
Iodine	I	53	126.932	Tin	Sn	50	118.70
Iridium	Ir	77	193.1	Titanium	Ti	22	48.1
Iron	Fe	26	55.84	Tungsten	W	74	184.0
Krypton	Kr	36	82.9	Uranium	U	92	238.17
Lanthanum	La	57	138.90	Vanadium	V	23	50.96
Lead	Pb	82	207.20	Xenon	Xe	54	130.2
Lithium	Li	3	6.940	Ytterbium	Yb	70	173.6
Lutecium	Lu	71	175.0	Yttrium	Y	39	88.9
Magnesium	Mg	12	24.32	Zinc	Zn	30	65.38
Manganese	Mn	25	54.93	Zirconium	Zr	40	91
Mercury	Hg	80	200.61				

Units and Standards.—It will be convenient here to define and record the numerical values of some of the terms used throughout the book. We shall use the centimeter-gram-

[1] *J. Am. Chem. Soc.*, **47**, 600 (1925). BAXTER, *J., Am. Chem. Soc.*, **48**, 541 (1926) gives 178.6 for hafnium, and suggests minor changes from the above values.

second system of units and the Centigrade temperature scale, most of the units of which are familiar from work in physics and chemistry.

A **liter** is the volume of 1000 grams of water at a temperature of 4°C.

A **kilo** is a thousand grams, and is the abbreviation of kilogram commonly employed.

A **mol** is the molecular weight of a substance in grams. This term is identical with gram-molecule or gram-molecular weight. As will be explained in the next chapter, this is the weight of gas which occupies the same volume as 32 grams of oxygen. It is sometimes defined as the weight of 22.4 liters of gas at 0° and 1 atmosphere.

A **calorie** is the quantity of heat required to raise a gram of water from 15 to 16°. It is abbreviated cal.; and the large calorie, which is a thousand small calories, is written Cal. A small calorie is 4.185 **joules,** or 4.185×10^7 **ergs.**

A **dyne** is the force which will impart to a gram mass a velocity of 1 cm. per second in a second. The acceleration of **gravity** at sea level and 45° latitude is 980.66. An **erg** is the work done by a force of 1 dyne acting through a distance of 1 cm.

Pressure is the force acting on a unit area. The absolute unit is 1 dyne per square centimeter, or one **bar.** A million bars is one **megabar,** which is very nearly the pressure of the atmosphere at sea level. Pressures are also commonly stated in atmospheres; a pressure of 1 **atmosphere** will support a column of mercury at 0°C., 76.00 cm. high at a point where the acceleration of gravity is normal, that is, at 45° latitude and at sea level. The force of 1 atmosphere is, therefore, $76.00 \times 13.60 \times 980.66 = 1{,}013{,}200$ bars, or 1.0132 megabars (13.60 being the mass of a centimeter cube of mercury at 0°). In spite of the convenient size of the megabar unit, which is more nearly the average atmospheric pressure than the standard atmosphere, the latter remains the common unit of pressure in scientific work. The adoption of the absolute unit has been strongly urged, but largely on account of the definition of boiling points and of the Centigrade temperature scale in terms of the standard atmosphere, the megabar has not come into common use.

The work done when a piston of 1-sq. cm. area moves 1 cm. against a pressure of 1 atmosphere is called a **cubic-centimeter-atmosphere.** This quantity of work is done for each cubic centimeter increase in volume during evaporation of a liquid at atmospheric pressure, that is, at the boiling point of the liquid. One small calorie is equivalent to 41.2 c.c.-atmospheres, or 1 c.c.-atmosphere is equivalent to 0.0243 cal.

Temperature is measured on the Centigrade scale, on which the melting point of ice under a pressure of 1 atmosphere is 0° and the boiling point of water under a pressure of 1 atmosphere is taken as 100°. The **absolute scale** (or Kelvin scale) consists of Centigrade degrees, but takes its zero point 273°[1] lower than the melting point of ice, for reasons explained in the next chapter. On this scale water, therefore, boils at 373°.

In chemical considerations the **formula weight** is a more convenient unit of quantity than the gram, and it is more definite than the chemical equivalent, which may be different for a substance taking part in different reactions. A formula weight of substance is that weight of it in grams which is the sum of the atomic weights of the elements in its chemical formula. Thus, 63.57 + 32.06 + 64 or 159.63 grams of $CuSO_4$ is a formula weight of the anhydrous substance, but 159.63 + 5 × 18.016 or 249.71 grams of the blue crystals make a formula weight of $CuSO_4.5H_2O$.

Concentration.—When a formula weight of a substance is dissolved in 1000 grams of solvent, a formal or molal solution results. This will not, in general, be exactly a liter of solution, even in the case of aqueous solutions, but a molal solution is defined in this way to facilitate calculating mol fraction (to be defined later) from concentration. We shall define a normal solution as in volumetric analysis: one containing a chemical equivalent of substance in a *liter of solution.* When the properties under consideration depend on the relative quantities of solvent and dissolved substance, molal concentrations will be employed. These are, in general, identical with formal concentrations, since the formula is written to correspond to the molec-

[1] BUCKINGHAM, *Bull. Bur. Standards,* **3,** 273 (1907) gives 273.13° as the melting point of ice on the Kelvin scale; KEYES (*J. Am. Chem. Soc.,* **42,** 4 (1920)) gives 273.14°; SMITH and TAYLOR (*J. Am. Chem. Soc.,* **45,** 2124 (1923)) find 273.12°.

ular weight. When the properties depend on the volume of the solution, normal or equivalent concentrations will be used. In dilute aqueous solutions a liter of solvent is contained in what is substantially a liter of solution, but the difference in volume between a solution and the solvent contained in it is often considerable for strong solutions.

A **coulomb** is an ampere-second, or that quantity of electricity which will deposit 0.00111800 gram of silver from solution in a standard coulometer. A **faraday** is 96,500 coulombs of electricity, and it will deposit one atomic weight of silver or its chemical equivalent of some other element.

An **ampere** is a current of 1 coulomb per second.

A **volt** is the electromotive force of a cell such that the electrical work done by it is 96,500 joules, or 23,074 cal., when the quantity of electricity passing through it is 1 faraday.

An **ohm** is such an electrical resistance that a potential of 1 volt across it causes 1 ampere current to flow; it is the resistance at 0° of a column of mercury 106.3 cm. long and 1 sq. mm. in cross-section.

Questions

1. The weight of a liter of hydrogen bromide at 0° is as follows:

Pressure	Weight of a Liter
1.0000	3.6441
0.6667	2.4220
0.3333	1.2074

Compute a value of d/p for each pressure, plot these values against the pressure, and extrapolate the curve. From its intercept on the axis of zero pressure calculate an exact value of the molecular weight of hydrogen bromide and of the atomic weight of bromine. The ideal molal volume at 0°C. is 22,410 c.c. and the atomic weight of hydrogen is 1.008.

2. From the atomic weight of bromine obtained in the previous problem calculate an exact value of the atomic weight of tin by means of the data in Table 3.

3. Assuming the atomic weight of silver to be 107.880, compute a value for the atomic weight of bromine from Table 1. Calculate the per cent deviation of this value from the one given in the International Table of Atomic Weights.

4. Potassium chlorate contains 39.154 per cent of oxygen, and a gram of silver when converted into silver nitrate will react with 0.691145 gram of

potassium chloride. (*a*) Calculate the molecular weight of potassium chloride and the atomic weight of silver from these data. (*b*) Calculate the atomic weight of chlorine from that of silver just found and the ratio of silver to silver chloride given in the text. (*c*) Calculate the atomic weight of potassium from the composition of potassium chlorate and this atomic weight of chlorine.

5. Silver bromate contains 20.35 per cent oxygen. Calculate the molecular weight of silver bromide. Calculate the atomic weight of bromine from the data of Table 1 and the atomic weight of silver obtained in the previous problem. Compare these values with those in Table 7.

6. Pure silicon tetrachloride was decomposed with sodium hydroxide solution, and the chloride was precipitated with silver nitrate made from weighed portions of silver. (*J. Am. Chem. Soc.*, **42**, 1194 (1920).)

Weight $SiCl_4$	Weight silver	Ratio $SiCl_4$:4 Ag
10.4353	26.4952	0.39386
5.9785	15.1830	0.39376
8.7905	22.3213	0.39381
6.8352	17.3562	0.39383

Calculate from each experiment the molecular weight of silicon tetrachloride, and calculate an average value of the atomic weight of silicon, using as the atomic weights of silver and chlorine 107.880 and 35.457. Calculate the percentage error in the value for silicon in the International table.

7. The following data (Morley) relate to the composition of water:

Weight hydrogen	Weight oxygen	Weight water
3.2559	25.8531	29.1052
3.8382	30.4700	34.3151
3.8523	30.5818	34.4327
3.8211	30.3429	34.1559

Calculate exactly the atomic weight of hydrogen from each set of weighings, and compare the average value with that in the International table.

8. Lead chloride is 74.545 per cent lead, and the heat capacity of lead is 0.029 cal. per gram. Calculate exactly the atomic weight of lead.

9. Cadmium bromide is 41.29 per cent metal. From these data and its specific heat, which is about 0.05, calculate its atomic weight, assuming Br = 79.92.

10. The ratio of hydrogen to bromine in hydrogen bromide is 1.000: 79.307. From this ratio and the atomic weight of hydrogen derived in question 7 calculate the atomic weight of bromine.

CHAPTER II

PROPERTIES OF SUBSTANCES IN THE GASEOUS STATE

A gas may be defined as a substance which distributes itself uniformly throughout any space in which it is placed, whatever quantity of gas is employed, and regardless of the amount of space. It should be kept in mind that a substance may or may not be a gas, according to the conditions imposed upon it. All of the substances which we commonly call gases have been liquefied at low temperatures; all except helium have been solidified. Nearly all of the common liquids and solids may be changed to the gaseous condition at high temperatures, and at low pressures. The exceptions to this statement are substances which decompose on heating. Substances such as the common metals, sodium chloride, and most metallic halides are readily changed to gases by heating to a high temperature; but nitrates and sulfates, complex organic compounds, and salts of organic acids generally decompose before reaching their temperature of vaporization.

When a quantity of gas cannot be separated into two fractions having different properties, such as density, solubility, or color, by any physical methods, it is a pure substance. It will be remembered that a pure substance is defined as one whose molecules are all exactly alike. Mixtures of two or more kinds of molecules exhibit in the gaseous state most of the physical properties of a gas containing only one kind of molecules; they follow the laws which describe the behavior of gases, and may usually be treated as a single gas. They should always be referred to as a mixture of gases, however.

Structure of a Gas.—On account of the ability of a gas to fill any quantity of space, it is necessary that the molecules of which it consists may be separated from one another with considerable ease. The fact that a small quantity of liquid gives a very much larger volume of vapor or gas at the same pressure is evidence that the molecules of a gas are separated from one another by considerable distances compared to the diameters of the molecules themselves. Eighteen grams of liquid water, or one molal

weight, occupy 18.8 c.c. in the liquid state at 100° and 1 atmosphere pressure, but these same molecules occupy about 30 liters when changed to a gas (steam) at this temperature and pressure. Thus in the gaseous phase[1] the volume available for the use of each molecule is over a thousand times what it was in the liquid state. We do not believe that the volume of the molecules themselves has changed in size to any considerable extent during evaporation, but only that the free space around them is larger. This will be taken up in more detail in connection with the kinetic theory of gases.

The molecules of a gas are not stationary, but are moving about in space with very high velocities. They "collide" with each other frequently and strike the walls of the containing vessel, giving rise to the pressure exerted by the gas. If the volume of the gas is increased, the number of molecular impacts on a given area is decreased, that is, a smaller number of molecules strike any area of the wall in a given time and the pressure decreases. The pressure of a gas at constant volume increases as the temperature is raised (Gay Lussac's law, page 27), which means that there are more collisions of the molecules with the walls in a unit of time, and hence that the velocity of the molecules increases at higher temperatures. The pressure exerted by a gas does not decrease with time, so we are led to the conclusion that the collisions between molecules are perfectly elastic and that no decrease in average velocity results from a collision. The "empty space" between molecules bears some resemblance to that between the spokes of a rapidly revolving wheel. The spokes do not fill all of the space in which they revolve at any

[1] The homogeneous parts of any system which are separated from one another by definite physical boundaries are often called its *phases*. For example, the homogeneous parts ice, liquid water, and water vapor are the phases or states of aggregation common to water. A solution is a single phase because there are no visible boundaries between the parts of it, solvent and dissolved substance. A mixture of several gases constitutes a single phase, for gases mix in all proportions, and there is no physical boundary between one gas and another. A mixture of solids forms as many phases as there are kinds of solid present, since each is divided from the others by definite boundaries. When a single solid substance is capable of existing in two different crystalline modifications, each of these is considered a separate phase. Rhombic and monoclinic sulfur, red phosphorus and yellow phosphorus, grey tin and white tin are familiar examples of pure substances forming two different solid phases.

one time, but the whole of this space is effectively occupied, so that nothing else can be kept in it. In the same manner, other molecules cannot be inserted into the "empty" space between molecules without increasing the number of collisions, and hence the pressure of the gas.

The treatment of gases at moderate pressures and at temperatures well removed from their condensation points is comparatively simple, for all of them have properties in common, which are expressed approximately by a few simple laws.

Boyle's Law.—This law states that at any constant temperature the volume occupied by a quantity of gas is inversely proportional to the pressure exerted upon it. While *all* substances undergo a decrease in volume with increasing pressure, it is only with gases that the volume is inversely proportional to the pressure or, as is commonly said, the "pressure-volume product" is constant at a given temperature. Very careful experiments made since the discovery of the law have shown that it is not very exact, but that it is a limiting law which describes the behavior of actual gases more closely as the pressure is decreased or as the temperature is raised. For gases under small pressures the deviations of Boyle's law are small, as shown by the following tables, and illustrated in Fig. 3.

TABLE 8.—HELIUM[1] AT 0°

Pressure in atmospheres	Volume of a molecular weight	Product
1.1021	20.65	22.41
1.0458	21.42	22.41
1.0020	22.37	22.41
0.9634	23.27	22.41
0.8067	27.78	22 41
0.7387	30.33	22.41
0.6847	32.73	22.41
0.6086	36.80	22.41
0.5387	41.61	22.41
0.4720	47.48	22.41
0.3550	63.10	22.41
0.2626	85.30	22.41
0.1937	115.65	22.41

[1] BURT, *Trans. Faraday Soc.*, **6**, 19 (1910).

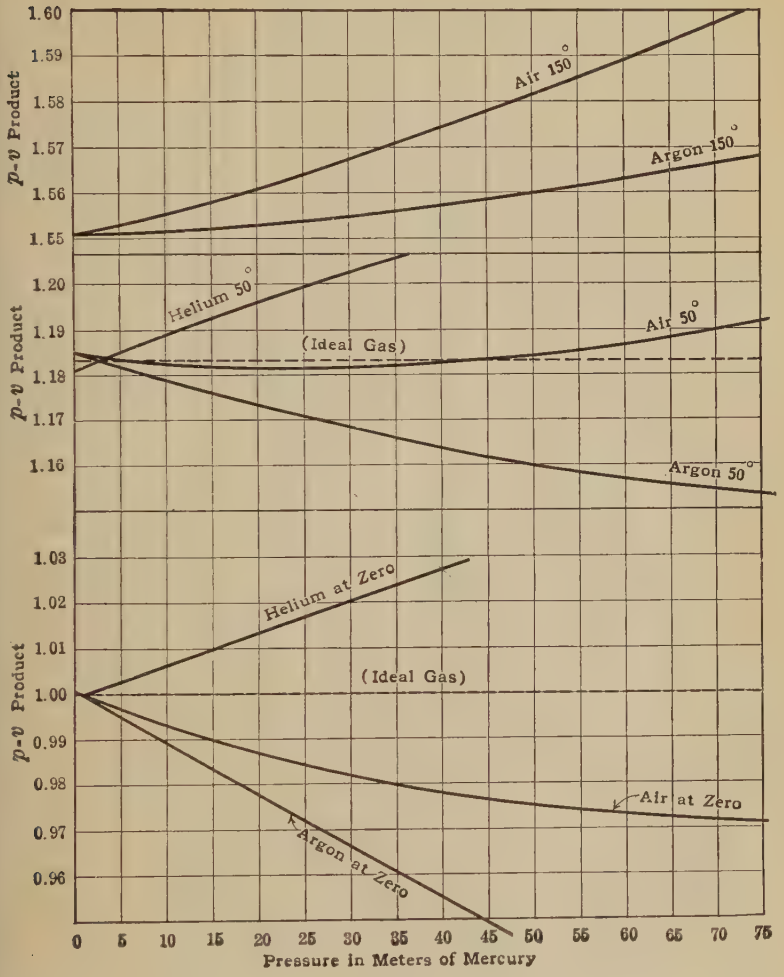
1.60
1.59
1.58
1.57
1.56
1.55
p-v Product
Air 150°
Argon 150°
1.20
1.19
1.18
1.17
1.16
p-v Product
Helium 50°
(Ideal Gas)
Air 50°
Argon 50°
1.03
1.02
1.01
1.00
0.99
0.98
0.97
0.96
p-v Product
Helium at Zero
(Ideal Gas)
Air at Zero
Argon at Zero
0 5 10 15 20 25 30 35 40 45 50 55 60 65 70 75
Pressure in Meters of Mercury

FIG. 3.

TABLE 9.—AIR AT VARIOUS TEMPERATURES[1]

Pressure (meters of mercury)	Pressure-volume product at				
	0°	50°	100°	150°	200°
0.76	1.0002	1.1838	1.3674	1.5508	1.7342
1	1.0000	1.1838	1.3674	1.5509	1.7344
5	0.9969	1.1830	1.3682	1.5525	1.7369
10	0.9934	1.1823	1.3693	1.5549	1.7403
15	0.9901	1.1818	1.3707	1.5578	1.7440
20	0.9870	1.1816	1.3724	1.5609	1.7480
25	0.9842	1.1816	1.3742	1.5641	1.7522
30	0.9817	1.1818	1.3762	1.5674	1.7565
35	0.9793	1.1822	1.3783	1.5708	1.7608
40	0.9773	1.1827	1.3806	1.5742	1.7651
45	0.9755	1.1833	1.3829	1.5777	1.7695
50	0.9740	1.1842	1.3854	1.5813	1.7739
55	0.9728	1.1852	1.3880	1.5849	1.7785
60	0.9720	1.1864	1.3908	1.5887	1.7831
65	0.9714	1.1880	1.3938	1.5927	1.7878
70	0.9712	1.1898	1.3970	1.5969	1.7927
75	0.9712	1.1918	1.4003	1.6013	1.7977

HELIUM AT VARIOUS TEMPERATURES

Pressure, meters of mercury	Pressure-volume product at		
	0°	50°	100°
0.76	0.9998	1.1827	1.3657
1	1.0000	1.1829	1.3659
5	1.0028	1.1856	1.3685
10	1.0062	1.1890	1.3718
15	1.0097	1.1923	1.3751
20	1.0132	1.1957	1.3784
25	1.0167	1.1990	1.3816
30	1.0202	1.2024	1.3849
35	1.0236	1.2057	1.3882
40	1.0271	1.2091	1.3915

[1] HOLBORN and SCHULTZ, *Ann. Physik*, **47**, 1089 (1915).

These data present what is perhaps the better side of the case. When gases with more complex molecules are concerned, or when the temperature of observation is close to the point at which condensation takes place, the deviations from Boyle's law become quite large. Some data[1] for such substances will be found on page 63 in connection with methods of allowing for these deviations in certain calculations. Thus when at 0° the pressure of carbon dioxide is actually 26.7 atmospheres, the value to be expected from the constancy of the pressure-volume product is 34.0, which is in error by over 27 per cent. Similarly, ether vapor at 220° has a calculated pressure-volume product which is 33 per cent in error when the pressure is 30 atmospheres. Hence some judgment is required in the application of Boyle's law, as is the case for the other gas laws about to be stated. But the law is true to within 1 or 2 per cent for most permanent gases under pressures up to about 10 atmospheres, at ordinary or high temperatures.

Law of Gay Lussac.—When a quantity of gas at 0°C. is heated while the volume is kept constant, the pressure increases a definite fraction of its value at 0° for each degree rise in temperature. This fraction is 0.003667, or 1/273 of the pressure at 0°. For example, if the original pressure at 0° were 1 atmosphere, it would be 1.003667 at 1°, 1.03667 at 10°, 1.3667 at 100°. Since this fractional increase per degree is 1/273, the pressure would reach 2 atmospheres at 273°. If the temperature were reduced until the pressure was one-half atmosphere, this temperature would be 273/2 degrees below zero. Thus at any temperature t the pressure is $(273 + t)/273$ times the pressure at 0°C.

Scale of Temperature.—By choosing as a temperature scale one composed of Centigrade degrees, with 273 as the melting point of ice (Centigrade zero), we would have a scale such that the pressure of a gas at constant volume is proportional to the temperature, for if the pressure is unity at 0°C. where the newly chosen temperature is 273, and it increases 1/273 of this pressure for every degree rise in temperature, it would be 2 atmospheres

[1] Data for other substances may be found in the Landolt-Börnstein Tables; in the Communications of the Physical Laboratory of the University of Leiden in Holland (available in English); in the tables published by the Smithsonian Institution; and in Volume III of the International Critical Tables.

at 273°C., and this temperature on the new scale is 273 + 273, or double the temperature corresponding to 0°C. This may be called a gas scale of temperatures; it is more often called the absolute scale or Kelvin temperature scale after the physicist of that name. There are reasons other than the temperature coefficient of expansion of gases for believing that −273°C. is an

TABLE 10.—CHANGE OF PRESSURE-VOLUME PRODUCT OF HELIUM WITH TEMPERATURE[1]

(A quantity of helium which at 0°C. and 1 atmosphere pressure was 1000 c.c. was subjected to various temperatures and pressures. Under pv are the observed pressures multiplied by the observed volumes. From these products and the weight of helium employed, 0.17850 gram, the value of pv/T for a mol of helium has been calculated and is shown in the last column. If the ideal gas law described accurately the behavior of helium, all of these values would be 82.0. The deviations are not due to experimental errors in the measurements; they show real deviations of the gas laws.)

Temperature, Centigrade	T absolute	Pressure in atmospheres	pv	$\frac{pv_m}{T}$
100.3	373.3	42.574	1387.25	83.2
		54.459	1393.14	83.5
		66.590	1399.29	83.9
20	293	27.539	1086.64	83.0
		36.303	1090.28	83.2
		53.708	1099.18	83.9
0	273	1.000	1000.00	82.0
		26.634	1013.92	83.0
		38.565	1018.50	83.5
		50.240	1025.21	84.1
−103.6	169.5	20.580	631.35	83.2
		24.100	632.96	83.5
		29.185	635.97	83.7
		33.383	638.45	84.1
−182.8	90.3	13.751	337.87	83.7
		16.019	338.98	83.9
		18.189	340.25	84.1
−216.56	56.5	9.564	211.32	83.7
		10.502	211.71	83.9
		11.448	212.19	83.9

[1] ONNES, *Comm. Phys. Lab. Univ. Leiden*, **102a** (1907).

"absolute zero" of temperature below which it is impossible to go by any means whatever. Some of these reasons will be given later in their proper place (Chapter IV). It will be sufficient for the present to consider that absolute temperatures are gas-scale temperatures; that is, temperatures such that the pressure-volume product for a quantity of gas is proportional to the temperature. This law, like Boyle's law, is not strictly true for gases at low temperatures (where condensation is possible) or at very high pressures, but it is the limiting law which describes the behavior of gases more and more closely as higher temperatures and lower pressures are employed. An example of actual experimental results is given in Table 10. To change Centigrade temperatures to absolute temperatures, add 273° to them.[1] In this book the usual custom of denoting these temperatures is followed, Centigrade temperatures by t, absolute temperatures by T. Thus $T = (273 + t)$ in every case.

Gas Thermometer.—Since the increase of the pv product is proportional to the absolute temperature for an ideal gas, and nearly so for an actual gas, a thermometer may be constructed on this principle. If a quantity of gas at constant volume has a pressure p_0 in melting ice, a pressure p_{100} when surrounded by water boiling at 1 atmosphere, and a pressure p_t at some unknown temperature t, then this temperature may be determined from the equation[2]

$$t = \frac{100(p_t - p_0)}{p_{100} - p_0}. \qquad (1a)$$

This expression is the quotient of $(p_t - p_0)$, the actual increase, and $(p_{100} - p_0)/100$, the increase of pressure per degree. That

[1] More exactly, 273.12 (see the footnote to page 19). A similar "absolute scale" for Fahrenheit degrees may readily be calculated. As stated above, if the pressure of a gas is 1 atmosphere at 32°F., it would be 1.3367 at 212°F. and constant volume. This corresponds to an increase of 0.3667/180 or 1/492 per Fahrenheit degree. Hence, on an absolute Fahrenheit scale "absolute zero" would be 492° below 32°F. or 460° below 0°F. Such a scale is often employed by engineers, and the temperatures $(t_F + 460)$ are called degrees Rankine. The temperatures −273°C. and −460°F. would be designated 0°K. and 0°R., respectively, and each would designate "absolute zero."

[2] Buckingham (*Bull. Bur. Standards*, **3**, 237 (1907)) discusses these equations in detail.

is, $(p_t - p_0)/(p_{100} - p_0)$ is the fraction of the increase per hundred degrees, and 100 times this fractional increase is the increase in temperature in degrees.

A corresponding set of measurements of the volume of a quantity of gas at constant pressure at the two standard temperature points and at an unknown temperature t leads to the expression

$$t = 100 \frac{v_t - v_0}{v_{100} - v_0}. \qquad (1b)$$

Except in work of the greatest precision, the deviations of these scales from true temperatures are not important when the gas employed obeys Boyle's law approximately. On the absolute scale we may write

$$\frac{T}{T_0} = \frac{v}{v_0} (p = \text{const.}) \text{ or } \frac{T}{T_0} = \frac{p}{p_0} (v = \text{const.}). \qquad (1c)$$

These scales are known respectively as the constant-pressure gas scale and the constant-volume gas scale. They both give true absolute temperatures to within small fractions of a degree. It should be noted that equation (1*c*) is true only if the expansion per degree is 1/273 of the volume at zero. This is not the case in equation (1*a*), where it is only necessary that the temperature coefficient of pressure increase at constant volume is the same throughout the temperature range 0 to 100°C.; that is, it is only necessary that dp/dt = a constant; or, using the integral of this expression, it is necessary that $p = kt + a$; equation (1*c*) requires that a is $273k$. For example, a gas which is not an ideal gas, but which is described by van der Waals' equation, to be given later, will give correct Centigrade temperatures when equation (1*a*) is employed, but will not lead to correct absolute temperatures through equation (1*c*).

Ideal Gas Law.—By combining the two laws just given we obtain the equation

$$\frac{pv}{T} = \text{const.},$$

where the numerical value of the constant depends on the units chosen for expressing p and v and on the quantity of gas under consideration. If we consider a "mol" of gas (*i.e.*, the molecular weight of it in grams) as the standard quantity, then the numerical value of the constant in a given set of units is independent

of the nature of the gas, and is usually denoted by R. The equation then becomes, for one mol of any gas,

$$pv_m = RT. \tag{2}$$

A *mol* of gas (or gram-molecular weight) is chosen as a unit in preference to a gram, since the molecular weight of any gas occupies the same volume as the molecular weight of any other gas. Then from the known value of the constant R which applies to all gases we may calculate the pressure or volume of a mol of any gas.

Since the volume of n mols of gas is obviously n times as great as the volume of one mol, the equation may be written so as to describe the behavior of any quantity of gas in terms of the one constant R,

$$pv = nRT, \tag{3}$$

where n is the number of molecular weights or mols of gas under consideration.

The numerical value of R depends only on the units chosen to express p and v. It should be noted that R has the dimensions of work, since the product pv is force per unit area $\times$ volume, or force $\times$ distance; and the quantities n and T are numbers. Suppose a cylinder of area a, fitted with a tight piston. When this piston moves through a distance h against a pressure of p on each square centimeter of the piston, the force exerted is pa, and it acts through the distance h; but since ah is the volume of the cylinder, pah is pv, and this has the dimensions of work.

Let us express p in dynes per square centimeter and v in cubic centimeters; and calculate the value of R from the density of oxygen. Morley[1] found that a liter of this gas at 0° and 76.0 cm. of mercury pressure weighed 1.4290 grams. Since the density of mercury is 13.60, the mass of the column of mercury supported on a square centimeter of gaseous surface is 13.60×76.0, and the force is the product of mass and the acceleration of gravity, or $13.60 \times 76.0 \times 980 = 1{,}013{,}200$ dynes per square centimeter. The value of n is $1.4290/32.00 = 0.0446$ mols. Substituting in equation (3) we have

$$\underset{p}{1{,}013{,}200} \times \underset{v}{1000} = \underset{n}{0.0446} \times \underset{R}{R} \times \underset{T}{273}$$

[1] *Smithsonian Contr. Knowledge*, **29**, 1–117 (1895).

whence

$$R = 8.316 \times 10^7 \text{ ergs} = 8.316 \text{ joules.}^1$$

If we wish to express R in terms of the cubic centimeter and atmosphere, then, using the same data

$$1.00 \times 1000 = 0.0446 \times R \times 273$$

and $R = 82.13$ c.c.-atmospheres[2] or 0.08213 liter-atmosphere. In later calculations it will be convenient to have the value of R expressed in heat units, calories. Since 1 cal. is 4.185 joules, $R = 8.316/4.185 = 1.99$ cal.[3]

Equation (3) describes the behavior of most gases under moderate variations in pressure and temperature with an accuracy of about 1 or 2 per cent. An **ideal gas** is one whose behavior would be exactly in accordance with this equation. No such substance is known, but all actual gases approach the condition of the ideal gas more closely as the pressure upon them decreases and as the temperature increases. The "ideal gas" is thus the limiting condition for all gases, and equation (3) is called the ideal gas law or ideal gas equation. The term "perfect gas" is also commonly employed in this connection, but "ideal" serves to keep constantly before us the imaginary character of such a substance. In a later section (page 59) we shall consider gases under conditions of high pressure and at temperatures near the condensation point, where the ideal gas laws do not apply even roughly in some cases. But for calculations at temperatures well removed from condensation points and at moderate pressures (up to 10 atmospheres, for example) the

[1] Some writers prefer to state the numerical values assigned to R as *joules per degree*, which values when multiplied by T result in joules. Against this practice no objection can be raised. However, as the c.g.s. system of units leaves temperature as a dimensionless quantity, the briefer notation of R in joules or ergs or calories will be followed in this book.

[2] A cubic-centimeter-atmosphere is the work necessary to move a piston of 1 sq. cm. area through a distance of 1 cm. against a pressure of 1 atmosphere. One small calorie is equivalent to 41.2 c.c.-atmospheres.

[3] The usefulness of equation (3) is not confined to the c.g.s. system of units. Pressure may be expressed in pounds per square foot and the quantity of gas in pound-mols. As explained on page 29, $t_F + 460 = T_R$, where the subscript R indicates the Rankine, or Fahrenheit absolute scale. Using this absolute scale, with pressure in pounds per square foot, volume in cubic feet, and quantity of gas in pound-mols, the value of the constant R in equation (3) is 1544.

deviations of gases from the equation $pv = nRT$ are commonly less than 2 per cent.

Much larger deviations usually indicate a change in the number of mols present. Of course, equation (3) cannot be expected to describe the changes of p or v with T if the number of mols present is also changing. For example, phosphorus pentachloride vapor partially decomposes according to the equation $PCl_5 = PCl_3 + Cl_2$, and the extent of the dissociation depends upon the temperature and pressure. On the other hand, simultaneous measurements of p, v, and T for a weighed quantity of such a material affords a ready means of determining the number of mols present for these conditions. A numerical example for the dissociation of phosgene ($COCl_2$) is given at the end of the next paragraph. Such "deviations" are really only examples of the misapplication of a law to conditions for which it was not derived and to which there is no reason to expect it to apply.

Mol Fraction.—A common method of expressing the composition of a mixture is in terms of the number of mols of each substance present, divided by the total number of mols of all substances present. As an example, the composition of the earth's atmosphere may be computed in terms of the mol fractions of the constituents. Analysis shows that 100 grams of air contain 23.25 grams of oxygen, 75.5 grams of nitrogen, and 1.24 grams of argon. On dividing each of these weights by the molecular weight of the substance in question we find 0.727 mol of oxygen, 2.70 mols of nitrogen, and 0.032 mol of argon, total 3.459 mols in 100 grams of air. The mol fraction of oxygen is, therefore, $0.727/3.459 = 0.210$, that of nitrogen is $2.70/3.459 = 0.781$, and that of argon is $0.032/3.459 = 0.009$.

A mol of a gaseous mixture is that quantity of it which occupies the same volume as 32 grams of oxygen under the same conditions of temperature and pressure.

At 20° and 1 atmosphere pressure the volume of 32 grams of oxygen is 24 liters. By mixing 5040 c.c. of oxygen, 18,745 c.c. of nitrogen, and 215 c.c. of argon, a total volume of 24,000 c.c. is obtained and the mixture has properties identical with those of air. The mixture contains 0.210 mol of oxygen, 0.781 mol of nitrogen, and 0.009 mol of argon, therefore a total of 1 mol. We may thus properly speak of this 24 liters of air as a mol of

air, though it contains less than a mol of any one substance. By multiplying the number of mols of each substance in a mol of air by its molecular weight and adding, we find that a mol of air weighs 29.0 grams. This "molecular weight of air" is useful in applying the ideal gas laws to air, and in calculating molecular weights of gases from the densities expressed as multiples of the density of air under the same conditions. For example, refer to the description of molecular weight determinations by the method of Victor Meyer (page 42).

The concept of mol fraction may be used to determine the extent of gaseous dissociation from measurements of density. For example, phosgene ($COCl_2$) dissociates to an extent which depends upon the temperature and pressure. At 550° and 1 atmosphere total pressure the weight of a liter of (partially dissociated) phosgene is 0.852 gram. At this temperature and pressure a molal volume is 67.4 liters. Hence a mol of mixture weighs $67.4 \times 0.852 = 57.4$ grams. If x is the fractional dissociation of phosgene, then each mol which dissociates will yield x mols of chlorine, x mols of carbon monoxide, and $1 - x$ mols of phosgene will remain, or a total of $1 + x$ mols for each formula weight of phosgene. The mol fractions in the mixture will be $x/1 + x$ for CO and for chlorine, and $(1 - x)/(1 + x)$ for un-dissociated phosgene. The weight of a mol of mixture is obtained by multiplying the mol fraction of each substance by its molecular weight as follows:

$$\frac{x}{1+x} \times 28 + \frac{x}{1+x} \times 71 + \frac{1-x}{1+x} \times 119 = 67.4$$

and upon solving this equation we obtain $x = 0.77$. This means that at 550° and 1 atmosphere pressure phosgene is 77 per cent dissociated into carbon monoxide and chlorine.

Dalton's Law.—This law states that in a mixture of gases each exerts its pressure independently of the others, or, in other words, the "partial pressure" of one gas is unaltered by the presence of another gas which also exerts a pressure. By partial pressure we mean that part of the total pressure due to the particular species of molecule under consideration. Obviously, the total pressure in any gaseous mixture must be the sum of the partial pressures of all the gaseous substances present. Dalton's

law may also be stated as follows: The partial pressure of any gas in a mixture of gases is proportional to the mol fraction of that gas. If p is the total pressure on a mixture of several components, a, b, c, . . .

$$p_a = px_a;\ p_b = px_b;\ p_c = px_c \ldots \qquad (4)$$

From this relation the mol fraction may be calculated if the partial pressure is known, or the partial pressure may be computed from a mol fraction determined by analysis. These calculations will be made frequently in the chapter on chemical equilibrium.

Suppose the three bulbs A, B, and C of Fig. 4 to be of equal volume and filled with oxygen, nitrogen, and hydrogen respectively, each under a pressure of 1 atmosphere. If the stop-cock b is opened and the hydrogen is forced from C into B (for example, by flowing mercury into C), the total pressure in B should rise to the sum of the two partial pressures, $p_H + p_N$. According to Dalton's law the pressure exerted by nitrogen on the walls of vessel B is still 1 atmosphere, or the same as its pressure when it was alone in the vessel. The law further requires that the partial pressure of the hydrogen be 1 atmosphere, since it is in a vessel of the same size as formerly. Direct experiment shows that the total pressure is, indeed, very close to 2 atmospheres as required by the law. If the contents of the middle bulb be now forced into vessel A, the total pressure should rise to 3 atmospheres; *i.e.*, $p_O + p_N + p_H = 3$.

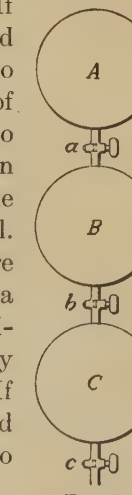

FIG. 4.

Table 11[1] on page 36 shows the percentage increase in volume when gases at 1 atmosphere pressure are mixed in varying quantities and the total pressure is kept at 1 atmosphere. All of the figures should be zero if Dalton's law were exact. It will be noticed that the deviations are all of the order of 1 or 2 per cent. Data by other observers indicate that these percentage errors may be too high; for example, Maass and Morrison[2] give the percentage increases in pressure shown in Table 12 when equal

[1] FUCHS, P., *Z. physik. Chem.*, **92**, 641 (1918).
[2] *Proc. Roy. Soc. Canada*, **18**, 49 (1924).

TABLE 11

Column 1 gives the volume of the gas first written at the head of each succeeding column in 100 c.c. of mixture. The other columns show the percentage increase in volume due to mixing, when the total pressure is kept at 1 atmosphere. As an illustration, when 20 c.c. of carbon dioxide and 80 c.c. of nitrogen are mixed, the resulting total volume is 101.96 c.c., but when 80 c.c. of carbon dioxide and 20 c.c. of nitrogen are mixed, the total volume is 101.46 c.c.

Volume per cent of first gas	Per cent increase in volume on mixing at 20°					
	$N_2O + N_2$	$CO_2 + N_2$	$N_2 + O_2$	$N_2O + CO_2$	$N_2O + O_2$	$CO_2 + O_2$
10	1.07	1.02	0.37	0.38	0.96	0.98
20	2.14	1.96	0.79	0.85	1.78	1.53
30	2.86	2.49	1.07	1.17	2.51	2.01
40	3.16	2.72	1.21	1.34	2.88	2.34
50	3.06	2.61	1.27	1.42	3.03	2.41
60	2.81	2.41	1.11	1.17	2.70	2.20
70	2.34	2.00	0.89	1.02	2.11	1.88
80	1.79	1.46	0.61	0.64	1.43	1.33
90	0.97	0.81	0.34	0.41	0.85	0.71

volumes of gases are mixed at a total pressure of 1 atmosphere. Masson and Dolley[1] find deviations for mixture of argon and ethylene which are about 2.5 per cent when the total pressure is 30 atmospheres.

TABLE 12.—INCREASE IN VOLUME ON MIXING

Gas mixture	Per cent increase in volume
Hydrogen—oxygen	0.075
Hydrogen—carbon dioxide	0.15
Hydrogen—carbon monoxide	0.026
Hydrogen—methyl ether	0.45
Oxygen—carbon monoxide	0.05
Carbon dioxide—carbon monoxide	0.18
Carbon dioxide—methyl ether	0.04
Carbon monoxide—ammonia	0.18

[1] *Proc. Roy. Soc.* (*London*) *A*, **103**, 528 (1923).

While it is difficult to state general rules, it will be observed that the volume changes are larger the more the components differ from one another in physical properties such as condensation point and in chemical structure. The maximum deviations occur in the presence of an excess of the gas with the lower critical temperature (page 81) in the mixture. When the gases approach each other in physical properties the maximum deviation from Dalton's law occurs in the 1:1 mixture; this is not true when the components differ considerably.

It has been possible in some cases to find materials which allow the free passage of the molecules of one gas but not of other gases, and thus to measure partial pressures directly.

Thus Ramsay[1] found that when a palladium bulb filled with nitrogen at 280° was surrounded by a stream of hydrogen the pressure within the bulb increased almost as much as the total

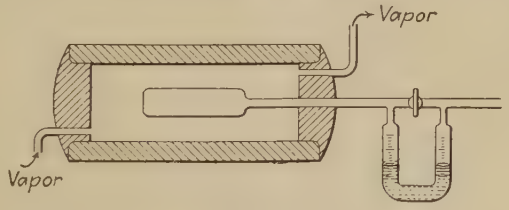

FIG. 5.

pressure of hydrogen outside of the bulb. His experiments were not continued until equilibrium was attained, and the partial pressure of hydrogen within the palladium bulb never reached the total hydrogen pressure outside. In a series of rather hasty experiments, he found that the partial pressure of hydrogen inside the bulb varied from 87 to 98 per cent of the pressure outside; and that the actual figure depended somewhat upon the condition of the palladium.

Lowenstein[2] made use of the permeability of platinum to hydrogen at higher temperatures in studying the extent of dissociation of water vapor. A platinum tube connected to an oil manometer was surrounded by water vapor contained in an electrically heated furnace, as shown in Fig. 5. As platinum allows the free passage of hydrogen molecules through it, but

[1] *Phil. Mag.*, **38**, 206 (1894).

[2] *Z. physik. Chem.*, **54**, 715 (1906).

not of oxygen or water vapor, the manometer should show the partial pressure of hydrogen. By means of this method it was found that at 1500° water vapor is about 0.1 per cent dissociated into hydrogen and oxygen.

Avogadro's Law.—The number of molecules contained in a given volume of ideal gas under any fixed conditions of temperature and pressure is independent of the nature of the gas. A more common statement of the law is that equal volumes of all gases under *standard* conditions of temperature and pressure contain the same number of molecules; but it should be made clear that so long as the two gases compared are at the *same* temperature and pressure, it is immaterial what the actual conditions are. The truth of this proposition was not conceded for a long time after it was put forth, and until recently its main support was the fact that the volumes of gases entering chemical reactions were simple whole multiples of each other and of the gaseous product formed. For example, since one volume of hydrogen and one of chlorine unite to form two volumes of hydrogen chloride without excess of either constituent remaining, it follows that the volume of hydrogen contained just the same number of particles as the volume of chlorine. Further, the number of molecules of hydrogen chloride is equal to the sum of the numbers of hydrogen molecules and chlorine molecules, for there are two volumes of gas after the reaction just as there were two volumes before it. Since no substance has ever been prepared which contained less chlorine per molecular weight than hydrogen chloride, it is natural to conclude that there is only a single atom of chlorine in each molecule of hydrogen chloride. The same reasoning holds for hydrogen. Thus it seems safe to state that the volume of chlorine contains the same number of molecules as the volume of hydrogen. It follows also that the molecules of hydrogen and chlorine each contain two atoms, for the molecules of hydrogen chloride all contain hydrogen, and two volumes of them resulted from the chemical combination of one volume of hydrogen.

Avogadro's Number.—Within recent years experiments have been made (some of which will be mentioned later in their proper place, Chaps. XIII, XV) from which it is possible to calculate the number of molecules in a gram-molecule. The

experiments have been performed by numerous investigators, using a variety of methods based on widely different phenomena, and among all of them the agreement is astonishing. Each of the methods has been subjected to searching tests, and it may be said with absolute conviction that the numbers found are true, in spite of the inconceivably large value of them. It would, of course, be quite impossible for any set of experimenters to count such numbers in a life time, but fortunately this has not been found necessary. All of the determinations are of the order of 6×10^{23}, or 600,000,000,000,000,000,000,000, and the molal volume of all gases contains this number of molecules.

In the following table are given some of the more recent determinations of this number, commonly called "Avogadro's number," or Avogadro's constant. A review of the experimental

TABLE 13.—AVOGADRO'S NUMBER[1]

Observer	Method	Molecules per gram-molecule
	Mean free path of a molecule	5 to 6×10^{23}
Perrin	Brownian movement of colloids	6.8
Svedberg	Intensity of Brownian motion	6.2
Brillouin	Intensity of Brownian motion	6.9
Fletcher	Rate of fall of oil drops in air	6.03
King[2]	Scattering of solar radiation	6.2
Pacini[3]	Scattering of solar radiation	5.7
Rutherford	Charge on an alpha particle	6.0
Millikan	Determination of unit electric charge	6.06 ± 0.01
Planck	Radiation laws	6.06
Perrin	Angular displacement of a colloidal particle	6.5
Boltwood	Alpha particles in helium from radium	6.3
Curie	Alpha particles from polonium	6.5
Rutherford	Kinetic energy of an alpha particle	6.2
Westgren[4]	Change of distribution of colloidal particles	6.09

[1] *Gen. Elec. Rev.*, **18,** 1159 (1915).
[2] *Trans. Roy. Soc. Canada,* **8,** 59 (1914).
[3] *Nuovo cimento,* **10,** 131 (1915).
[4] *Arkiv Mat. Astron. Fysik,* **13,** 14 (1918).

methods on which these determinations are based would be beyond the scope of this book, since the experimental procedures are usually complex, and the calculations in connection with them are somewhat involved.[1] There is an agreement among them which would be gratifying if the same method had been used by all the observers; when it is considered that the determinations have been made by methods which are quite different in principle, to say nothing of the apparatus used, the concordance is truly remarkable and convincing.

Among these determinations that of Millikan is perhaps the most accurate, and it may be said with certainty that we know the "population" of a gram-molecule as accurately as we know that of any large city. Probably no human mind is able to grasp the meaning of such an exceedingly large number as this, but a clear concept of its size is fortunately not required in order to benefit from the truth of Avogadro's law. The actual determination of the number is important to us chiefly as real tangible proof of the law. Indeed, the table shows such agreement among the experiments quoted (which are by no means all of the researches made in this field, but only selected examples) as to leave little doubt of the validity of the law. The actual determination of the number was accomplished about a hundred years after the first statement of the law (1811) by Avogadro.

Viewed in the light of this number the attainment of a "vacuum" seems quite hopeless, for the lowest pressures ever measured, after the most efficient removal of gas from a container, are about 0.001 dyne per square centimeter (this is approximately $\frac{1}{100,000,000}$ of an atmosphere), and in this "vacuum" the number of molecules per cubic centimeter is greater than the population of the earth.

Molecular Weight Determinations—Direct Method.—When the ideal gas equation is written $pv = \frac{m}{M}RT$, it will be seen that the molecular weight M of a gas may be determined when the weight m of a known volume at some definite temperature and pressure is known. A glass bulb of 300- to 500-c.c. capacity is

[1] Brief descriptions of several of the methods have been given in four popular lectures by RUTHERFORD, *Engineering*, **119**, 296, 326, 358, 410 (1925); and by DUSHMAN, *Gen. Elec. Rev.*, **18**, 1159 (1915).

evacuated and carefully weighed, then filled at a fixed temperature and pressure with the gas under consideration and weighed again. The data on page 12 were obtained by this method.

Dumas' Method.—If the substance whose vapor density is desired is a liquid at room temperature, about 10 c.c. of it may be placed in a weighed bulb of the form shown in Fig. 6. All of the bulb except its tip is then immersed in a constant-tempera-

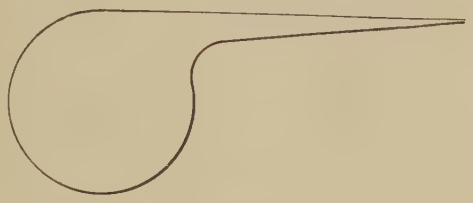

FIG. 6.

ture bath (usually boiling water) and the air and excess liquid are expelled from the bulb. When all of the liquid has been vaporized, the bulb is sealed and the barometer is read. At the moment of sealing, the bulb is filled with vapor at the barometric pressure and at the temperature of the bath. Thus T and p are known, m is determined by weighing the sealed bulb again, and v by filling the bulb with water and weighing again. As the bulb when first weighed is filled with air which is expelled by the boiling liquid, it is necessary to compute the weight of air expelled and subtract it from the first weighing in order to obtain the weight of the empty bulb alone. Some results obtained by a slight modification of this method are shown in Table 14.[1]

Actual data on carbon tetrachloride may be used to illustrate the method of calculation.

	GRAMS
Bulb (filled with air)	51.43
Bulb with CCl_4 vapor	53.20
Bulb filled with water	411

The difference between the weight of the bulb when filled with water and the weight filled with air is 360 grams, and this is substantially the volume of the bulb in cubic centimeters. The weight of air contained in the bulb at its first weighing was not present at the second weighing. Its weight may be obtained by

[1] SCHULTZE, *Physik. Z.*, **14**, 922 (1914).

TABLE 14.—MOLECULAR WEIGHTS BY DUMAS METHOD

Substance	Temperature	Weight of a liter of vapor	Molecular weight found by experiment	Formula weight
Ether	70°	2.634	74.15	74.08
Ether	80°	2.560	74.13	74.08
Ether	90°	2.485	74.03	74.08
Carbon disulfide	80°	2.687	77.84	76.14
Acetone	80°	2.010	58.22	58.05
Benzene	95°	2.583	78.01	78.05
Chloroform	95°	3.986	120.40	119.40
Alcohol	95°	1.522	45.97	46.05
Methyl alcohol	95°	1.065	32.17	32.03
Hexane	95°	2.853	86.15	86.11
Ethyl acetate	95°	2.919	88.16	88.06
Nitrobenzene	250°	2.882	123.70	123.10

substituting in the equation $pv = nRT$, from which it will follow that 0.015 mol of air, or 0.43 gram, was present. The empty bulb, therefore, weighed 51.00 and hence 2.20 grams of carbon tetrachloride vapor filled the volume of 360 c.c. and exerted a pressure of 1 atmosphere at 100°C. when the bulb was sealed. Upon substituting these values in $pv = (m/M)RT$, M is found to be 156.

The divergences between experimentally measured molecular weights and those calculated from the formula of the substance are not due to errors in the experiments themselves, but to a failure of the ideal gas equation to describe accurately the behavior of the vapor. Such deviations can be eliminated from this method to a large extent by the "limiting density" procedure mentioned on page 12 of the previous chapter.

Victor Meyer's Method.—This procedure is adapted to substances which vaporize at somewhat higher temperatures than those suited to Dumas' method; indeed, it can be applied at all temperatures below the softening point of glass. In principle the method consists in vaporizing a weighed quantity of the liquid or solid substance in a vessel filled with hot air at such a temperature that the substance vaporizes readily. The hot

bulb is made much larger than the volume which the substance will occupy as a vapor, and when vaporization takes place a volume of air equal to that of the vapor formed is expelled into a measuring vessel. In other words, hot vapor has been substituted for an equal volume of air at the high temperature prevailing in the bulb, and the air is then cooled for convenience in measuring.

One form of Victor Meyer apparatus is shown in Fig. 7. The substance whose molecular weight is desired is weighed in a sealed bulb *a* with a capillary stem bent as shown in Fig. 7[1] and supported upon a rod *b*. If the bulb has thick walls and is not completely filled, it will not burst in the furnace, even at 75° above its boiling point. The part of the apparatus enclosed within the dotted line is maintained at a constant temperature 25 to 50° above the boiling point of the substance. When the temperature has become constant, the pinchcock *e* is closed and the capillary stem of the bulb is crushed against the tube *d* by raising the rod *b*. The bulb falls into the heated portion of the vaporizing chamber *c*, where the substance evaporates, and displaces an equal volume of air from the top of the chamber. This air is collected in the buret and measured. It represents the volume which the vaporized substance would have at the temperature of the buret if it were a gas at this temperature. Knowing the barometric pressure and the temperature in the buret, we have all of the necessary data for substituting in the equation $pv = (m/M)RT$, and the molecular weight M is readily

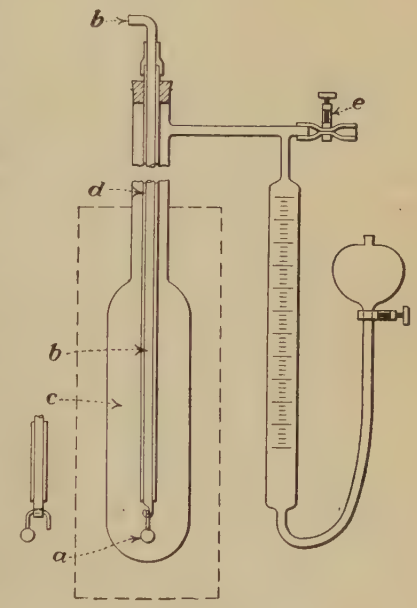

FIG. 7.

[1] MACINNES and KREILING, *J. Am. Chem. Soc.*, **39**, 2350 (1917).

calculated. The temperature used in this calculation is that of the gas in the buret, not the temperature of the vaporizing chamber; for the vaporized substance has displaced a volume of hot air equal to its volume while hot, and this air has been cooled for convenience in measurement. Some typical results are shown in Table 15.

TABLE 15.—MOLECULAR WEIGHTS OBTAINED BY THE VICTOR MEYER METHOD[1]

(Bromine, formula weight 159.8)

Weight taken	0.1970	0.2015	0.1475	0.2059	0.1861
Vol. air displaced	30.33	30.15	22.71	31.05	29.00
Buret temperature (abs.)	297	298	296	298	298
Pressure (corr. for aqueous tension in the buret)	735	735	735	755	729
Mol. wt. calcd	164	164	163	167	164

	Alcohol, formula weight 46.05			Ether, formula weight 74.1		
Weight taken	0.0494	0.0612	0.0561	0.1023	0.1159	0.0971
Volume air displaced	27.23	33.68	30.54	35.33	40.40	33.68
Buret temperature (abs.)	297	297	297	306	307	305
Pressure (corr.)	725	725	725	733	733	733
Mol. wt. calcd	45.9	46.4	46.4	75.7	75.3	74.9

The experimental results are uniformly higher than the accepted values which accord with the simple molecular formula. This is to be expected since all of the substances have large molecules, the vapors in the heated bulb are at pressures which are not far removed from the condensation pressures, and the molecular weights were calculated from the simple gas laws. If the results are calculated from the van der Waals equation (for example), they will be found much closer to the accepted formula weights. That is, the differences are due to the failure of the law of ideal gases to describe accurately the behavior of the vapor. Since molecular weights are used largely to supplement accurate analytical data, for which purpose rough determinations suffice, calculations are ordinarily based on the ideal gas law.

[1] MACINNES and KREILING, *J. Am. Chem. Soc.*, **39**, 2350 (1917).

KINETIC THEORY OF GASES

Fundamental Equation.—The molecules of a gas are not at rest, but move about through the confining space with great rapidity,[1] colliding frequently with each other and with the walls of the vessel surrounding them. This statement is supported by the fact that when two gases are brought in contact and the mixture is allowed to stand, it finally becomes homogeneous, or of uniform composition throughout. If a quantity of chlorine be placed in the bottom of a vessel by displacing part of the air in it, a distinctly greenish layer will be seen. If this is allowed to stand for some time, the green layer diffuses upward throughout the whole vessel, and there is no longer any visible boundary between the two gases. This mixing is not dependent on stirring; it will take place if the vessel is kept absolutely quiet and at a constant temperature, in spite of the different densities of the gases.

The pressure exerted on the walls of a container by a gas is entirely due to collisions which take place between the moving molecules and the walls. It is known that the pressure does not decrease if a gas is allowed to stand indefinitely in a closed space at constant temperature, and that a gas does not continuously absorb heat from the surroundings to supply the energy of motion of its molecules. This can be true only if the molecules are perfectly elastic as regards their collisions with one another, for otherwise the collisions would absorb energy and the intensity of motion would gradually decrease and cause the pressure to fall off. The pressure is perfectly constant on all the walls at all times, so the bombardment of the walls must be uniformly distributed.

Within a gas the molecules move about in the utmost chaos, with no regularity whatever, and at widely different velocities. A molecule which has a high velocity at one instant may suffer a collision which changes its direction and velocity at any moment. Indeed, the path of each molecule is absolutely haphazard, and the state of a gas must be thought of as absolute confusion.

[1] The molecules in air move at about ⅓ mile per second, but the average straight-line distance traveled between collisions is only about 0.0001 cm., thus making the number of hits per second for each molecule about five thousand million.

But it is convenient in visualizing the behavior of molecules, as regards pressure exerted on the surrounding walls, to consider their motions along three axes perpendicular to the faces of a confining cube; and to consider the mean[1] velocity of all the molecules, in place of the rapidly changing velocity of a single molecule.

Let us consider that the molecules, in place of moving about in chaos, move in three directions perpendicular to the faces of a cube, and that one-third of them move in each of the directions at any moment of time. This is equivalent to resolving the actual motions into their components along three perpendicular axes and considering the motion in one direction at a time. Let m be the mass of a single molecule moving in one direction with a velocity u_1 cm. per second, and let the side of a cube containing the gas be l. In order for a molecule to make a complete round trip from a given point to one wall, then to the other wall, and back to the starting point, it must travel the distance $2l$, which will require $2l/u_1$ secs. To state this in another way, the molecule will make $u_1/2l$ round trips per second, and hence strike a given wall of the vessel $u_1/2l$ times per second. This molecule

[1] By applying the laws of probability Maxwell has shown that the distribution of velocities among a large number of molecules which have a given mean velocity is shown by the equation

$$y = \frac{4}{\sqrt{\pi}} x^2 e^{-x^2},$$

where y denotes the probability of a velocity whose magnitude is x, the most probable velocity being taken as unity. Figure 8 shows this curve graphically. The arithmetic average velocity is 1.13 times the most probable velocity; and the "mean" velocity is 1.22 times the most one. By "mean" is meant the velocity which would give the average probable kinetic energy. This is, therefore, the square root of the average of the squares, or root-mean-square velocity, and is denoted by u in the above text.

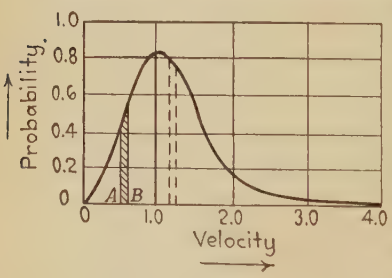

FIG. 8.

Since the area under the curve is unity, the fraction of all of the molecules which have velocities between OA and OB is denoted by the shaded area. For a further discussion of these matters see DUSHMAN, *Gen. Elec. Rev.*, **18**, 952 (1915).

pproaches a wall with velocity u_1 before the collision, and after ts collision the velocity is $-u_1$. Its momentum is then changed rom mu_1 to $-mu_1$, and this takes place at the wall every time a nolecule strikes it.

The total change in momentum of this molecule at a given vall per second is, therefore, $2mu_1 \times u_1/2l$. Now let n be the umber of molecules in the cube, and let u be the mean velocity. We have already assumed that one-third of the molecules noved in each of the three directions. The change in momentum per second at one wall of the cube for all of the $n/3$ molecules triking it will be

$$2mu \times \frac{u}{2l} \times \frac{n}{3} = f,$$

r mu^2/l for each of the $n/3$ molecules. The force f exerted on a vall is the rate at which momentum is imparted to it,[1] so this xpression is equal to the force exerted by the gas on a wall of the ube. Pressure is by definition the force exerted upon a unit rea and the area of the wall is l^2, whence

$$p = \frac{f}{l^2} = \frac{1}{l^2} \times 2mu \times \frac{u}{2l} \times \frac{n}{3} = \frac{1}{3}\frac{mnu^2}{l^3}. \qquad (5)$$

But l^3 is the volume of the cube, which we will call v, and our quation then becomes

$$p = \tfrac{1}{3}\frac{mnu^2}{v}. \qquad (6)$$

ince for a mol of gas pv is equal to RT (equation (3)) we may rite

$$pv_m = \tfrac{1}{3}mnu^2 = RT, \qquad (7)$$

which is the fundamental equation of the simple kinetic theory. f p is in dynes per square centimeter (bars), v is in cubic centi- neters, m is in grams and u in centimeters per second, n is vogadro's number ($6.06 \times 10^{+23}$), and R has the value 8.32×0^7 ergs. Since mn equals M, the molecular weight, this equa- ion may also be written

$$pv_m = \tfrac{1}{3}Mu^2 = RT. \qquad (7a)$$

Validity of the Equation.—In deriving this equation we have ssumed that the molecules of a gas move perpendicular to

[1] Force has the dimensions, ml/t^2, and momentum is ml/t, hence $(ml/t) \times /t$ is the rate of imparting momentum to a surface.

the faces of a cube with a mean velocity u, whereas they move about in inconceivable confusion and strike the walls at all possible angles and with velocities varying from zero to very high values. Ordered motion could not possibly be established in the three directions and (owing to collisions) would not remain ordered for a finite length of time if established. Hence a reasonable suspicion of the validity of the equation thus derived may exist, and it must justify its existence by according with the known behavior of gases or be valueless. Let us examine the case for and against our equation.

In perfectly random motion among a very large number of molecules, with millions of millions of collisions taking place, the same number of impacts would probably fall on each face of the cube in a given time, and among such a large number of perfectly random hits, they would probably be distributed about uniformly over the area; our assumption was an equal number of collisions on each wall, uniformly distributed over it. If we resolved the motion of each molecule in the totally chaotic state along three perpendicular axes at any given instant of time, we would find the same average velocity resolved on each axis, otherwise the pressure exerted on the different walls would not be the same, and this is contrary to experimental evidence. Our assumption is that equal velocities are resolved along each axis.

If we write equation (7) in the form

$$\tfrac{2}{3}n \times \tfrac{1}{2}mu^2 = RT$$

it will be seen that since $\tfrac{2}{3}n$ is constant for a molal volume (Avogadro's law), $\tfrac{1}{2}mu^2$ must be the same for all gases at a given temperature, since nothing has been assumed as to the kind of molecule concerned. An experimental proof of this fact is outlined below in the section relating to the effusion of gases.

When two different gases at the same temperature are mixed, there is almost no change in temperature; this holds for all temperatures. Consequently, the average kinetic energy of the molecules ($\tfrac{1}{2}mu^2$) must be practically the same for all gases at the same temperature and must increase at the same rate for all gases. All of these statements are in agreement with the known behavior of gases.

If the kinetic energy of a gas molecule depends only on its emperature and is independent of the nature of the gas,

$$pv = \tfrac{2}{3} \cdot \tfrac{1}{2} m_1 u_1^2 n_1 = \tfrac{2}{3} \cdot \tfrac{1}{2} m_2 u_2^2 n_2.$$

f $p_1 v_1 = p_2 v_2$ at a given temperature, the same volume of the wo gases must contain the same number of molecules, *i.e.*, $_1 = n_2$, since $\tfrac{1}{2} m_1 u_1^2 = \tfrac{1}{2} m_2 u_2^2$, and this is the law of Avogadro. Thus we see that our fundamental equation (7) is in substanal agreement with all the known facts concerning gaseous ubstances at moderate pressures, even though we have made ther broad assumptions in its derivation. Evidently these ssumptions, while contrary to the *mechanism* of the processes ccurring in a gas, lead to the same consequences as the actual perations taking place.

The equation may, in fact, be derived without assuming that he molecules have regular motion in given directions, and by king into account the varied velocities shown at a given instant y the molecules, but such a derivation is beyond the scope of an lementary book. Students just beginning the study of physical hemistry will do well to concern themselves with the simpler rivation given above and the usefulness of the correct final uation (7) as an aid in forming a concept of the kinetic state a gas, rather than to attempt a rigid derivation. They should rhaps view the "derivation" above as an attempt to make uation (7) appear plausible, and consider the agreement of ductions based on it (such as Graham's law of effusion, and e specific heat equation for monatomic gases given below) th experimental facts as "proof" of its validity. Certainly the markable agreement between the derived specific heat values d those determined in a calorimeter constitutes a sufficient stification for the existence of the equation; and it will materily aid us in forming a conception of the nature of a gas.

Rate of Effusion of Gases.—At any given temperature the netic energies of two kinds of molecules should be the same cording to our equation, that is,

$$\tfrac{1}{2} m_1 u_1^2 = \tfrac{1}{2} m_2 u_2^2$$

$$\frac{u_1}{u_2} = \sqrt{\frac{m_2}{m_1}} = \sqrt{\frac{M_2}{M_1}} = \sqrt{\frac{d_2}{d_1}}, \qquad (8)$$

since the masses of the molecules are proportional to the molecular weights M_1 and M_2, and to the densities d_1 and d_2. This equation states that the velocity of the molecules should be inversely proportional to the square root of the density of the gas. Since effusion through a small hole is a manifestation of molecular motion, the correctness of this equation may be tested by comparing the rates of effusion of gases through a given opening. The statement in equation (8) is, in fact, Graham's law of effusion of gases. Some of his data are here quoted to show that this consequence of the fundamental equation (7) is proved by experiment.

TABLE 16.—RATE OF EFFUSION OF GASES[1]

Gas	Density relative to air	Time of effusion relative to air	Square root of density	Velocity of effusion relative to air	Velocity calculated from square root of density
Air.....	1.0000	1.000	1.0000	1.000	1.000
Oxygen	1.1056	1.053	1.0515	0.950	0.951
N_2.....	0.9714	0.984	0.9856	1.016	1.015
CO.....	0.9678	0.987	0.9838	1.012	1.016
CH_4....	0.5549	0.765	0.7449	1.322	1.342
CO_2. ...	1.5290	1.218	1.2350	0.821	0.809
N_2O....	1.5290	1.199	1.2350	0.834	0.809

The following calculations will illustrate the method of applying equation (8) under a small (constant) driving pressure. Suppose that 100 c.c. of air will flow through a pinhole in a thin plate in 75 sec. and that under the same conditions 100 c.c. of another gas escape in 92 sec. Since the faster moving molecules will escape at a higher rate, the velocities are inversely proportional to the relative times of escape, and equation (8) may be written

$$\frac{t_2}{t_1} = \sqrt{\frac{M_2}{M_1}}.$$

Upon substituting 75 sec. as t_1, 92 sec. for t_2, and 29 for M_1, it is found that M_2 is 44. The second gas was carbon dioxide, whose molecular weight is 44.

[1] GRAHAM, *Phil. Trans. Roy. Soc. London*, **136**, 573 (1846).

or the molecular heat capacity at constant pressure is

$$C_p = \tfrac{5}{2}R = 4.97 \text{ cal. per degree.} \qquad (12)$$

As mentioned above, this equation is applicable only in case energy is not used in increasing the rotation of the molecules, in causing their vibrations to increase, or in any other way than in increasing the kinetic energy of the molecules. At the time this equation was first developed the only monatomic gas known was mercury vapor, and it was considered a triumph of the kinetic theory that the molal heat capacity of this substance was equal to that required by equation (12). Since that time five other monatomic gases, the so-called rare gases of the atmosphere, have been discovered and subjected to experiment. As shown by the following table, these substances have the heat capacity to be expected from the kinetic theory of gases. It is, indeed, a useful equation from which we can predict the heat capacity of a substance before it has been discovered.

TABLE 17.—MOLAL HEAT CAPACITIES OF MONATOMIC GASES

Substance	C_p	$C_p - R = C_v$	Experiments by
Mercury vapor	4.97	2.98	Kundt and Warburg
Helium	5.10	3.11	Behn and Geiger
Argon	4.99	3.00	Niemeyer
Argon	4.97	2.98	Pier
Argon	5.07	3.07	Heuse[1]

[1] *Ann. Physik,* **59,** 86 (1919).

The work done when a gas expands at constant pressure is substantially R cal. for each degree increase in temperature, whether the gas is monatomic or not, for in obtaining the expression for this work we used only the equation $pv_m = RT$ and this applies to a mol of gas whether its molecules are monatomic or diatomic; that is,

$$C_p - C_v = R$$

holds for any gas for which $pv_m = RT$ holds.

Ratio of the Specific Heats at Constant Pressure and at Constant Volume.—In addition to the evidence derived from experi-

ments on the temperature change during expansion into a vacuum (to be discussed presently), there is another way in which the correctness of equations (11) and (12) may be tested. It will be remembered that these equations were derived on the assumption that all of the energy added to the gas increased the kinetic energy of the molecules, or performed work in overcoming the pressure of the atmosphere during expansion. Let us assume for the moment that there is some unknown absorption of energy in addition to those stated. The equation $C_p - C_v = R$ has been established by experiment; and the quantity of energy $\frac{3}{2}R$ must be absorbed to increase the kinetic energy of the molecules and account for the experimentally proved increase in pressure with the temperature. Let x denote the energy required for the unknown uses mentioned above. Then the ratio of specific heats at constant pressure and at constant volume is

$$\frac{C_p}{C_v} = \frac{\frac{5}{2}R + x}{\frac{3}{2}R + x} = \frac{5R + 2x}{3R + 2x}.$$

It is possible to determine the ratio of these two specific heats from the velocity of sound in a gas,[1] and the ratio for monatomic gases is 1.667. Now this is $\frac{5}{3}$, and hence x in the above equation must be 0. This shows that the equations derived above are supported by the results of experiment.

Heat Capacity of Diatomic Gases.—In case the molecules of a gas contain more than one atom, considerable quantities of energy may be absorbed in producing rotation of the molecule, or in producing internal vibrations, *i.e.*, displacement of one of the atoms relative to another. Experiment shows that the pressure of the diatomic and triatomic gases increases with the absolute temperature in the same way as that of the monatomic gases, which could be true only if the kinetic energy of the molecules increase with the temperature in the same way. The energy absorbed and converted into vibrations or rotations must therefore be in addition to that required to increase the

[1] The equation for this ratio is

$$\textit{sound velocity} = n\lambda = \sqrt{(p/d)\gamma}, \qquad (13)$$

where n is the frequency or "pitch" of the sound, λ is its wave length, p and d are, respectively, the pressure and density of the gas, and γ is the ratio C_p/C_v for the gas in which the sound travels. It was derived by Laplace.

kinetic energy of the molecules, and in addition to that required o do work against the atmosphere during expansion. Let us lenote this additional energy by the term "internal energy," neaning thereby all of the energy absorbed which is not used in ncreasing the kinetic energy of the molecules or in external work. Then

$$C_p = \tfrac{3}{2}R + R + E_{\text{int}}$$

nd

$$C_v = \tfrac{3}{2}R + E_{\text{int}}.$$

TABLE 18.—RATIO OF THE MOLAL HEAT CAPACITIES OF GASES AT CONSTANT PRESSURE TO THOSE AT CONSTANT VOLUME[1]

Gas	Centigrade temperature	C_p	C_v	C_p/C_v
Argon	15	5.07	3.07	1.65
	−180	5.31	3.01	1.76
Carbon dioxide	20	8.88	6.85	1.30
	−75	8.07	5.90	1.37
Nitrous oxide	20	9.24	7.20	1.28
	−30	8.79	6.71	1.31
	−70	8.37	6.23	1.34
Nitric oxide	15	7.25	5.25	1.38
	−45	7.17	5.16	1.39
	−55	7.26	5.25	1.38
	−80	7.33	5.31	1.38
Methane	15	8.50	6.50	1.31
	5	8.42	6.41	1.31
	−30	8.14	6.12	1.33
	−55	8.08	6.05	1.34
	−80	8.08	6.03	1.34
Acetylene	18	10.43	8.38	1.25
	−70	9.13	6.96	1.31
Ethylene	18	10.22	8.18	1.25
	−36	9.17	7.08	1.30
	−68	8.79	6.63	1.33
	−91	8.64	6.41	1.35
Ethane	15	12.40	10.33	1.20
	−35	11.04	8.90	1.24
	−82	10.44	8.15	1.28

[1] HEUSE, *Ann. Physik*, **59**, 86 (1919).

It will be seen from these equations that the ratio C_p/C_v will be smaller than $\frac{5}{3}$ in case E_{int} has a considerable value. Table 18 shows that this ratio is much smaller than 1.667; it is about 1.4 for diatomic gases, and it approaches unity as a limit as the internal energy increases in comparison to the increase of kinetic energy. Thus for ether, a gas molecule containing 15 atoms, the ratio[1] is only 1.08. Equations expressing the results of experimental data on the heat capacity of actual gases will be found in Chap. VII.

Mass of Gas Striking a Unit of Surface.—As shown on page 47, pressure is the force exerted on unit area, which is the momentum imparted to the area in unit time. If m is the mass of gas striking 1 sq. cm. each second and u is the mean velocity of the molecules, $2mu$ is the pressure caused by these molecules. The velocity is given as a function of the molecular weight and temperature in equation (7a), from which u is equal to $\sqrt{\frac{3RT}{M}}$. This leads to the expression

$$p = 2m\sqrt{\frac{3RT}{M}}, \text{ or } m = \tfrac{1}{2}p\sqrt{\frac{M}{3RT}},$$

where m is the mass of gas in grams striking a unit of surface, p is the pressure of the gas in dynes per square centimeter, M is the molecular weight of the gas, T is the absolute temperature, and R has the value 8.32×10^7 ergs. Langmuir[2] has derived a more exact expression for the mass of gas striking a unit area during each second, by taking into account the distribution of velocities around the most probable one as mentioned on page 46.

[1] From the law of the equipartition of energy it can be shown that the heat capacity of a gas is $\frac{1}{2}R$ for each "degree of freedom" of its molecules. A diatomic molecule has three degrees of directional freedom (motion along the three axes) and two degrees of rotational freedom, about the two perpendicular axes which are each perpendicular to the line joining the centers of the atoms of the molecule. Thus the heat capacity of oxygen at constant volume should be $\frac{5}{2}R$ and at constant pressure $\frac{7}{2}R$, whence the ratio would be 1.40. These figures are in good agreement with the measured values recorded in the table. That the matter is not so simple as this is shown by an increase of the molecular heat capacity with the temperature. For this variation no simple explanation is known.

[2] *Phys. Rev.*, **2**, 329 (1914).

His equation differs from the one above only by a numerical constant. The exact equation is

$$m = p\sqrt{\frac{M}{2\pi RT}}. \qquad (14)$$

We may illustrate the application of this equation by calculating the mass of oxygen striking each square centimeter of a surface exposed to air under ordinary conditions. The partial pressure of oxygen is 0.21 atmosphere, or 21.2×10^4 dynes per square centimeter; T is 293 for a Centigrade temperature of 20°, and the other quantities have been given above.

$$m = 21.2 \times 10^4 \sqrt{\frac{32}{2 \times 3.14 \times 8.32 \times 10^7 \times 293}},$$

whence m is 3.1 grams per second.

Energy Absorbed during Expansion When No Work Is Done. In the above derivation of the specific heat equation for monatomic gases at constant pressure (equation (12)) it was assumed that all of the energy added was changed into the kinetic energy of the molecules or used in overcoming the external pressure. There are other ways in which energy might be used, and unless the quantity so used is zero, equation (12) is not applicable. For example, if the molecules exert considerable attractive forces on one another, these forces will resist the expansion, and they must be overcome during expansion. If an experiment could be arranged in which no work was done during expansion, it would be possible to measure the energy required for the separation of the molecules against their own attractive forces, should these exist. Suppose one of the bulbs in Fig. 10 to be filled with a gas and the other to be evacuated, both being in a vessel of water containing a sensitive thermometer. When the stop-cock is opened, gas will rush into the empty bulb and the pressure in the first vessel will fall until it is the same in both bulbs. The gas does no external work in expanding into the vacuum, but the molecules of the gas are separated from each other. If

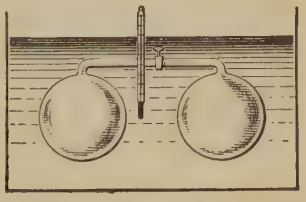

Fig. 10.

energy is absorbed in this separation, it must come from the gas itself or from the water in the calorimeter vessel, either of which would be shown by a change in the reading on the thermometer.

Joule-Thomson Effect.—Experiments which were better arranged to detect this cooling effect have shown that there is no appreciable decrease in temperature when the pressure of the expanding gas is small. Under higher pressures, the molecules of gases come close together, and exert larger attractions on each other. If such an expansion be carried out from high pressures, there will be a considerable decrease in temperature during the expansion, called the Joule-Thomson effect. If very sensitive measuring instruments be employed, small cooling effects may be observed with ordinary gases at moderate pressures. For monatomic gases the cooling effect has been found to be negligible, and equation (12) leads to values for the heat capacity of these gases which are in strict agreement with experiment. In the following table are shown some figures which illustrate the Joule-Thomson effect[1] for a pressure decrease of about 3 atmospheres.

TABLE 19.—COOLING OF GASES ON EXPANSION

Gas	Initial temperature	Observed cooling
Carbon dioxide	0°	4.82°
	40°	3.47°
	80°	2.90°
Oxygen	10°	1.07°
	90°	0.80°
Air	7°	0.88°
	90°	0.51°
Nitrogen	8°	1.03°
	90°	0.63°
Hydrogen	7°	−0.10°
	90°	−0.148°
	−80°	0.00°

[1] BUCKINGHAM, *Bull. Bur. Standards*, **3**, 237 (1907).

Liquefaction of Gases.—At high pressures the cooling effects discussed above become more considerable. If the expansion takes place adiabatically, that is, so that no heat is absorbed from the surroundings, and the cooled gas is caused to flow back around the high-pressure pipe, progressive cooling will take place until a portion of the entering precooled gas liquefies. In modern apparatus for liquefying air, the cooling from the Joule-Thomson effect is supplemented by allowing the expanding gas to perform work at the expense of its heat content.

Deviations from the Simple Gas Laws.—The simple law $pv = RT$ no longer applies when the pressure is increased to quite high values, or when the gas approaches the temperature at which it condenses to a liquid under the applied pressure. The compressibility is less than that called for by this simple law; that is, doubling the pressure does not decrease the volume to half its original value. It is natural to conclude that compression does not change the volume of the molecules, but only decreases the free space between them. At high pressures, the volume occupied by the molecules becomes considerable in comparison with the total volume of the system. A better representation of the observed compressibility is obtained by modifying the equation to allow for the volume of the molecules, by writing it, for one mol,

$$p(v_m - b) = RT,$$

where b is understood to be about the volume occupied by a mol of molecules. It is perhaps the volume which the molecules would occupy if brought to rest; certainly it is not smaller than this, and it may be larger. Let us consider it as that part of the volume which is not compressed by increasing the pressure on the gas. By subtracting the incompressible volume b from the observed total volume v_m we bring our equation into better accord with the facts.

Effect of Molecular Attraction—van der Waals' Equation.—It may be seen from Table 19 that the molecules do attract each other and that the cooling, which may be assumed a measure of the attraction, is different for different substances. This attraction tends to bring the molecules closer together, just as does the applied pressure; it should, therefore, be added to the pressure term to show that both the applied pressure and this

"internal pressure," A, are compressing the gas. Our equation now stands, for a mol of gas,

$$(p + A)(v_m - b) = RT.$$

A further inspection of the table will show that the attractive pressure, or internal pressure, decreases as the temperature is raised, therefore as the volume is increased by this rise of temperature. It is thus evident that the attractive pressure is a function of the molal volume itself. This is supported by the known fact that the deviations of actual gases from the simple law $pv_m = RT$ become smaller as the pressure becomes smaller, whereas if A is a constant, its importance would become greater relative to p at lower pressures. If we consider the layer of molecules about to strike a given wall at any instant of time, we see that the attraction holding them back will be proportional to the number of molecules back of them, *i.e.*, to the number of molecules attracting them. Since the number about to strike at any instant is also proportional to the number present, it follows that this attractive force is proportional to the square of the density of the gas, or inversely proportional to the square of the volume occupied by a mol of gas. Our equation may then be written with $a/^2v$ in place of A, when we have

$$\left(p + \frac{a}{v_m^2}\right)(v_m - b) = RT. \qquad (15)$$

This is the equation of van der Waals for the behavior of a mol of gas, though the argument on which it is based is not the same as that used in its original derivation. In this form the equation is able to represent quite accurately the behavior of gases under much higher pressures than those to which the equation $pv_m = RT$ is applicable; but it is, of course, much more difficult to handle. Unlike the simple gas law equation, it contains constants which depend on the nature of the gas under consideration. The quantities a and b are different for different gases, and must be calculated from experiments on the particular gas under consideration; these values are shown in Table 20.

Ethyl ether has a specific volume of 28.48 c.c. per gram at 303°C. when the observed pressure is 20.4 atmospheres. The molal volume is obtained by multiplying 28.48 by the molecular weight of ether, which gives 2120 c.c. per mol. Using the values

of a and b in Table 20 we may calculate from equation (15) that the pressure is 20.3 atmospheres. Application of the ideal gas law, $pv_m = RT$, in this case gives 22.3 atmospheres. Thus the pressure calculated from van der Waals' equation is about 0.5 per cent in error, while that calculated from the ideal gas law is 9.3 per cent in error.

TABLE 20.—VALUES OF VAN DER WAALS' CONSTANTS a AND b WHEN THE PRESSURE IS IN ATMOSPHERES, AND THE MOLAL VOLUME IN CUBIC CENTIMETERS[1]

Substance	b c.c. per mol	a	Value of the attractive force a/v^2 at a molal volume of 1 liter (atmospheres)
H_2	0.23	0.19×10^6	0.19
O_2	31.6	1.36×10^6	1.36
N_2	37.3	1.31×10^6	1.31
CO_2	42.8	3.61×10^6	3.61
CO	38.6	1.43×10^6	1.43
SO_2	56.5	6.69×10^6	6.69
C_2H_6	69.9	6.0×10^6	6.0
C_6H_6	120.3	18.71×10^6	18.7
CCl_4	127.3	20.86×10^6	20.9
H_2O	33.2	5.87×10^6	5.87
Ether	128	16.0×10^6	16.0
NH_3	36.4	4.05×10^6	4.0

The equation of van der Waals also applies to the liquid state of substances; that is, it describes the compressibility of a liquid and its change of volume with changing temperature, though in a less satisfactory way than with gases. Near the critical region (the highest temperature at which condensation to a liquid is possible) the equation fails completely. It will be recalled that in the derivation we did not assume that the attraction between the molecules varied as any particular function of the distance between the molecules; we assumed only that the attractive force

[1] For other data see *Z. physik. Chem.*, **69**, 52 (1910); and pages 253–263 of Landolt-Börnstein's Tables (1923). Since the unit of volume used in these tables is a molal volume at 0° and 760 mm., the values of a given there should be multiplied by $(22{,}400)^2$ and those for b by 22,400.

was dependent on the number of molecules. A proper knowledge of the change of forces acting between molecules with the distance between them will doubtless explain some of these deviations.

When the pressure becomes small and the volume of a mol of gas correspondingly large, the term a/v_m^2 becomes so small in comparison with p that it may be neglected; also the volume b is negligible in comparison with the molal volume v_m, and it may be neglected. The equation of van der Waals thus reduces to the simple gas law at large molal volumes.

Richards[1] states that the quantity b is about 1.2 times the molal volume of the liquid substance at its boiling point, and that it represents essentially the volume of the molecules themselves. Others incline to the view that b is somewhat larger than the volume of the molecules, perhaps four times as large. The point has not yet been settled definitely.

Other Equations for Gases.—The equation of van der Waals is not by any means the only equation which has been proposed to represent the changes of pressure and temperature of a gas with volume; many others have been suggested from time to time, and new ones are constantly being proposed. In general, it may be said that the accuracy with which a given equation expresses the behavior of an actual substances increases somewhat as the complexity of the equation employed increases, though this is not necessarily true. For a compressed gas is a highly complex system in which must be considered the attraction and repulsion of molecules for one another, the variation of these forces with the temperature, the variation of the volume of the molecules themselves with temperature, etc. It is not surprising that a simple equation is unable to take all of these features into account.

One recent equation which accords quite accurately with observed experimental data is that of Keyes,[2] which may be written

$$\left(p + \frac{a}{(v_m - l)^2}\right)(v_m - \delta) = RT, \qquad (16)$$

where a and l are constants and the logarithm of δ is a function

[1] *J. Am. Chem. Soc.*, **36**, 629 (1914).

[2] F. G. Keyes, *Proc. Nat. Acad. Sci.*, **3**, 323 (1917).

of the volume. Calculations based on this equation are rather difficult to carry out, but the agreement between observed and calculated pressures is excellent.

TABLE 21.—PRESSURE OF CARBON DIOXIDE AT VARIOUS VOLUMES.[1] SHOWING DEVIATIONS OF PRESSURES CALCULATED FROM THE IDEAL GAS LAW, FROM VAN DER WAALS' EQUATION, AND FROM KEYES' EQUATION, FROM EXPERIMENTAL PRESSURES

Abs. temp.	Volume of a mol	Measured pressure, atmospheres	Calculated pressures and percentage deviations					
			Ideal gas law	Per cent	van der Waals	Per cent	Keyes	Per cent
273	1,320	15.07	17.0	13	15.4	2	15.10	0.2
	1,100	17.70	20.4	15	18.2	3	17.69	0.0
	880	21.22	25.5	22	22.1	4	21.33	0.5
	660	26.67	34.0	27	28.0	5	26.72	0.2
304	1,320	17.22	18.9	10	17.4	1	17.23	0.1
	1,100	20.32	22.7	12	20.6	2	20.30	0.1
	880	24.58	28.4	15	25.2	3	24.68	0.5
	660	31.36	37.9	20	32.1	2	31.41	0.2
321	1,320	18.40	19.9	8	18.5	1	18.40	0.0
	1,100	21.75	24.0	10	21.9	1	21.72	0.1
	880	26.41	30.0	14	26.8	2	26.52	0.5
	660	33.92	40.0	18	34.3	1	33.97	0.2
337	1,320	19.50	20.9	7	19.5	0	19.48	0.0
	1,100	23.08	25.1	9	23.1	0	23.05	0.1
	880	28.13	31.4	11	28.3	1	28.23	0.5
	660	36.31	41.9	13	36.5	1	36.36	0.2
373	1,320	21.98	23.1	5	21.9	0	21.95	0.2
	1,100	26.11	27.8	7	25.9	1	26.07	0.2
	880	32.01	34.7	8	31.9	0	32.11	0.4
	660	41.74	46.3	11	41.3	1	41.78	0.1

In Table 21 are shown the pressures of carbon dioxide corresponding to temperatures and molal volumes there given, together

[1] F. G. KEYES, *Am. Soc. Refrigerating Eng.*, **1916,** Dec. 4.

with the pressure calculated from the ideal gas law $pv_m = RT$; from van der Waals' equation, using the values of a and b given in Table 20; and from Keyes' equation, together with the percentage deviation of each of these calculated pressures from the experimental one. It should be noted that pressures calculated from the ideal gas law are seriously in error, and that this error is smaller for lower pressures and for higher temperatures. The deviations of van der Waals' equation are less serious, but are also smaller when the observed pressures are small and the temperature is high.

Molecular Diameters.—The quantity b in van der Waals' equation represents about the volume occupied by the molecules themselves. A rough idea of the volume of a single molecule can be obtained by dividing the volume b, in cubic centimeters per molecular weight, by Avogadro's number; from which by extracting the cube root we obtain a measure of the diameter of a molecule. Two other equations of the kinetic theory, which are too complex to be considered here, also give a measure of the molecular diameter; one from measurements of the index of refraction of the gas, the other from calculations of the length of path of a molecule between collisions at small pressure. The results of these three methods agree remarkably, as will be seen[1]

TABLE 22.—MOLECULAR DIAMETER IN CENTIMETERS, AS CALCULATED FROM EQUATIONS OF THE KINETIC THEORY OF GASES

Gas	From the average free path of a molecule	From the value of b in van der Waals' equation	From the index of refraction of a gas
H_2	2.4×10^{-8}	2.34×10^{-8}	1.9×10^{-8}
He	1.9×10^{-8}	2.65×10^{-8}	1.17×10^{-8}
NH_3	2.97×10^{-8}	3.08×10^{-8}	.....
H_2O	.....	2.89×10^{-8}	2.28×10^{-8}
CO	3.19×10^{-8}	3.12×10^{-8}	2.52×10^{-8}
N_2	3.15×10^{-8}	3.15×10^{-8}	2.42×10^{-8}
O_2	2.97×10^{-8}	2.92×10^{-8}	2.32×10^{-8}
A	2.87×10^{-8}	2.94×10^{-8}	2.36×10^{-8}
CO_2	3.36×10^{-8}	3.23×10^{-8}	2.78×10^{-8}
Hg	.....	3.02×10^{-8}	.....

[1] DUSHMAN, *Gen. Elec. Rev.*, **18**, 1049 (1915).

from Table 22. Other methods of estimating the diameter of single molecules will be taken up in later chapters, where they will be seen to be in good agreement with the figures derived from the kinetic theory.

The value of b for ethane is 70 c.c. per mol. On dividing this by 6×10^{23} we obtain 115×10^{-24} c.c. as the volume of a single molecule. The cube root of this figure is roughly 5×10^{-8} cm., which is the diameter of a single molecule. The figures of Table 22, and those obtained by quite different methods in Chapter III, are all of this order of magnitude.

Questions

1. Calculate the volume of a mol of helium at 100° and a pressure of 65 cm. of mercury.

2. Calculate the temperature at which a liter of helium under a pressure of 1 atmosphere weighs a gram.

3. A liter of gas at 20° and 1 atmosphere pressure weighs 2.66 grams. Calculate the molecular weight of the gas.

4. At what pressure will ammonia gas have the same density as air at 1 atmosphere, if the temperature is the same for each?

5. What would be the volume of a balloon having at 20° a lifting power of a ton (910 kilos) if it is filled with hydrogen? Assume the molecular weight of air to be 29.

6. Water gas is practically a mixture of equal mols of carbon monoxide and hydrogen. Calculate the weight of a liter of it under standard conditions. Calculate its lifting power in a balloon, in kilos per cubic meter of gas.

7. When air is passed over hot coke and cooled to the original temperature, the volume increases 6 per cent. Assuming that no oxygen remains, calculate the mol fraction of CO_2 and of CO in the gaseous mixture. What will be the molal weight of the mixture? Air may be assumed 21 mol per cent oxygen and 79 mol per cent nitrogen.

8. At 250° and 1 atmosphere PCl_5 is 80 per cent dissociated into chlorine and PCl_3. Calculate the weight of a liter of the mixture under these conditions.

9. When steam is blown through carbon at a red heat, 80 per cent of it is converted into CO and hydrogen ("water gas"). Calculate the weight of a cubic foot of this gas at the mouth of the producer, where the temperature is 500° and the pressure is 1 atmosphere. What is the partial pressure of each gas? A cubic foot is 28 liters.

10. The pressure in an incandescent light bulb is about 1 dyne per square centimeter. If the gas in it is air, what is the weight of it in a 200-c.c. bulb? Calculate the actual number of molecules in the bulb. Assume a temperature of 20°.

11. Calculate the velocity of the oxygen molecules in air at 15°. Calculate the velocity of the nitrogen molecules.

12. At what temperature is the velocity of the oxygen molecules a mile per second? At what temperature is the velocity of hydrogen molecules 1 mile per second? (A mile is 1610 meters.)

13. (*a*) If 100 c.c. of nitrogen under a constant pressure will flow through a given orifice in 155 sec., what is the density of a gas of which 100 c.c. under the same pressure will flow through the same orifice in 175 sec.? (*b*) Assuming the gas to be a mixture of nitrogen and argon, calculate the mol fraction of argon in it. (*c*) Calculate the time of flow for a mixture in which the mol fraction of the nitrogen is 0.50.

14. Calculate the mass of carbon dioxide striking each square centimeter per second when the pressure is 0.001 atmosphere and the temperature 25°.

15. A liter of helium at 0°C. and 1 atmosphere pressure weighs 0.1785 gram. Calculate a value of the gas constant R.

16. (*a*) Calculate the pressure at which carbon dioxide has a molal volume of 1100 c.c. at 0°, employing the ideal gas law; and calculate this pressure from van der Waals' equation, using the values of a and b given in Table 20. (*b*) The observed pressure under these conditions is 17.70 atmospheres. Calculate the percentage error in each of the calculated pressures.

17. Make the same calculations as in question 16 for a temperature of 100°. The observed pressure at this temperature is 26.1 atmospheres.

18. Calculate the heat required to raise the temperature of 25 grams of helium through 100° at constant volume; at constant pressure.

19. What is the partial pressure of NO_2 in a mixture containing 45 per cent of it by weight and 55 per cent of N_2O_4? What is the apparent molecular weight of the mixture?

20. A dry Dumas bulb open to the air weighs 25.12 grams at 20° and 1 atmosphere. After expelling the air by boiling out a volatile liquid, and sealing at 100°, it weighs 25.358 grams. Filled with water, the bulb weighs 225 grams. (*a*) Calculate the molecular weight of the substance. (*b*) It contains 84 per cent of an element. What is the upper limit of atomic weight of this element?

21. A capsule containing 0.392 gram of selenium was dropped into a Victor Meyer bulb at 700°, and it expelled 33.2 c.c. of air, measured at 20° over water. (*a*) Calculate the apparent molecular weight. (*b*) Selenium vapor dissociates, $Se_6 = 3Se_2$. Calculate the partial pressures of Se_6 and Se_2 in the vapor at 700° and 1 atmosphere.

22. When 1.74 grams of Cl_2 and 1.57 grams of SO_2 are introduced into a 750-c.c. bulb at 190°, partial union into SO_2Cl_2 takes place and the pressure becomes 2 atmospheres. (*a*) Calculate the density of the mixture. (*b*) Calculate the partial pressure of each substance at equilibrium.

23. The vapor of acetic acid consists of a mixture of double and single molecules. A liter bulb at 220° and 1 atmosphere contains 2.55 grams of this vapor. (*a*) Calculate the fractional association. (*b*) Calculate the partial pressure of the double molecules.

24. When 0.315 gram of iodine is dropped into a Victor Meyer tube at 210°, a quantity of air is expelled which measures 30.2 c.c. over water at 25°. Calculate the molecular weight of iodine.

25. A capsule containing 0.200 gram of naphthalene is dropped into a Victor Meyer tube at 250° and it expels 39 c.c. of air, measured over water at 25° and 1 atmosphere total pressure. What is the molecular weight of naphthalene?

CHAPTER III

PROPERTIES OF SUBSTANCES IN THE LIQUID STATE

All of the substances which we were considering in the previous chapter as "gases," more properly termed substances in the gaseous state, may be changed to liquids by suitably increasing the pressure and lowering the temperature. A sufficient reduction in temperature will cause a gaseous substance to liquefy regardless of the pressure, unless this is kept exceedingly small; but, in general, an increase of pressure will not cause a substance to liquefy regardless of the temperature. There is a certain "critical temperature" characteristic of each substance, above which its gaseous phase may not be liquefied, no matter how great the pressure exerted upon it. Similarly, nearly all of the familiar liquid substances may be changed to the gaseous state at higher temperatures or under low pressures. The liquid phase, therefore, like the gaseous phase, depends upon the temperature and pressure for its existence.

Liquids are characterized by a greater resistance to flow (greater viscosity), by a much larger cohesive pressure, by a greater density and smaller compressibility than the same substances possess in the gaseous state. All of these changes are due to the much smaller distances between molecules; indeed, the molecules in a liquid are probably touching each other a considerable portion of the time. These molecules exhibit the same kind of thermal vibrations that were considered under the kinetic theory of gases, but the molecules have less freedom of motion. They have shorter paths between collisions, the motions are seriously affected by the attractive forces acting between the molecules, which are much more powerful in virtue of the smaller distances separating the molecules, but the *kinetic energy* of their motion is the same as that in the gaseous state at the same temperature.

Miscibility.—While gases are capable of mixing with one another in all proportions, and without influencing the properties

of each gas (such as its partial pressure), this is not true of liquids in all cases. Some pairs of liquids, such as alcohol and water, chloroform and carbon tetrachloride, benzene and xylene, do mix in all proportions; other pairs, such as aniline and water or ether and water, mix only to a limited degree; still others, such as benzene and water, alcohol and mercury, do not dissolve in each other to an appreciable extent. In the gaseous state all of these substances mix in all proportions, but this is doubtless because of the great separation of the molecules and the consequent lack of strong forces acting between them. In the liquid state, where molecules are very close to each other, specific attractive forces act between them, and these forces seem to govern the extent to which one liquid will dissolve in another. No general rules for solubility of liquids are free from exceptions, but it is usually true that liquids of the same chemical type (two hydrocarbons, two liquid metals, or water and alcohols) are soluble in each other, while liquids of quite different natures exhibit slight attractions for each other. Thus when benzene dissolves in toluene, its surrounding molecules are like it, and the attractive forces between molecules are not much altered. But, due to the great difference between benzene and mercury, there is no attraction between these molecules, and no mercury molecules separate from their own phase and enter the benzene phase. Mercury is, therefore, insoluble in benzene.

Molecular Attraction.—In the simple gas law, it was assumed that there were no attractive forces acting between the molecules; and it was found that at high pressures this assumption was not correct. To allow for it, a term (a/v^2) was introduced into the gas equation (van der Waals' equation). A molecular weight of water at 20° occupies about 18 c.c., and consists of the same molecules which form the vapor. But without the attractive forces which cause the vapor to condense (that is, assuming that water vapor was an ideal gas) the pressure necessary to bring a mol of gas into a space of 18 c.c. is given by $p \times 18 = 82 \times 293$, whence the pressure is 1340 atmospheres. The pressure exerted by water at 20° (its vapor pressure) is only about 0.02 of an atmosphere. It appears that the attractive pressure, or *internal pressure*, must, therefore, be very large. The cause of molecular attraction is not fully understood, but is believed to be due to

stray electric fields caused by the electrons within the atoms. Whatever its cause, its existence is certain, and new researches dealing with it are rapidly clearing up some of the disputed points.

Many equations have been put forward by various investigators for calculating the internal pressure of a liquid from a/v^2, from the latent heat of evaporation, and from other data. But the internal pressures so calculated are not in good agreement with one another in most cases. The following table shows the internal pressure[1] in atmospheres according to the calculations of various workers. It should be borne in mind that all of these calculations are based on certain assumptions, and that the actual internal pressure has not been measured directly. The deviations among the values for any one liquid will indicate the uncertainty of the assumptions made as to the way in which the attractive forces act; but all of the calculations agree in showing that there is an internal pressure, and that it is very great.

TABLE 23.—INTERNAL PRESSURE (IN ATMOSPHERES) OF VARIOUS LIQUIDS

	Winther[2]	Traube[3]	Walden[3]	Lewis[4]	Mathews[5]
Ether	1,220	990	1,360	1,930	1,970
Ethyl acetate	1,490	1,140	1,730	2,640	2,460
CCl_4	1,820	1,305	1,680	2,520	2,660
Benzene	1,790	1,380	1,920	2,640	2,940
Chloroform	1,680	1,410	1,950	2,780	2,910
CS_2	2,200	1,980	2,400	2,920	3,950
Ethyl alcohol	2,030	2,160	4,000	.....	3,600

[2] From optical properties.

[3] From surface tension and van der Waals' a and b.

[4] From thermal data.

[5] From latent heats and surface tension.

Surface Tension.—When a wire ring is dipped into a liquid, a continuous film of liquid may form within it, due to the attraction between molecules in the liquid. In the bulk of liquid this force is exerted equally in all directions, but molecules in a surface exert a force which has a resultant *in* the surface layer. This same force of attraction holds a drop of liquid suspended on a

[1] HILDEBRAND, *J. Am. Chem. Soc.*, **38**, 1459 (1916).

rod, and limits the size of a drop which may be so held; it causes the suspended drop to assume a spherical shape and thus reduce its surface to a minimum. Surface tension is measured in dynes per centimeter. If a ring has within it a continuous film of liquid, the surface tension causes a certain force to be directed toward the center of the ring for each centimeter of ring circumference. It is not correct to speak of surface tension per square centimeter, for such a force could not act within the surface, but outside it. The force here concerned is in dynes per centimeter length of surface film, it acts within the plane of the surface, and perpendicular to the direction in which the length of film edge is measured.

The rise of a liquid in a capillary tube which is wet by the liquid may be used as a measure of its surface tension. If γ is the tension in dynes per centimeter, and h is the height to which a liquid of density d rises above the horizontal surface in a tube of radius r, the equation connecting these quantities is

$$\gamma = \frac{rhdg}{2}. \qquad (1)$$

This equation results from equating the surface tension to the weight of liquid raised by it when equilibrium of forces is reached. The length of film edge is the circumference of the tube, $2\pi r$, hence the force is $2\pi r\gamma$, and this is balanced by a volume of liquid $\pi r^2 h$ of density d acted upon by the force of gravity g. It follows from this that $2\pi r\gamma = \pi r^2 hdg$, and upon solving for γ, equation (1) results.

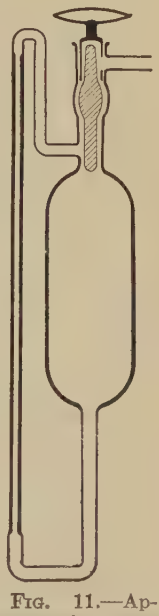

FIG. 11.—Apparatus for measuring capillary rise.

Much of the data on surface tension measured from the rise in capillary tubes is in error[1] on account of failure to measure the height h above a *horizontal* surface. The tube in which the flat surface is measured should be at least 3 cm. in diameter in order to have a horizontal surface in it; smaller tubes exhibit a capillary rise of their own which renders a capillary rise relative to such a surface incorrect. Richards' apparatus is shown in

[1] RICHARDS, *J. Am. Chem. Soc.*, **37**, 1656 (1915).

Fig. 11. The height of capillary rise[1] is measured with a cathetometer by focusing on the horizontal surface in the large bulb, then on the capillary meniscus in the tube connected to the bulb. Some measurements by this method are shown in Table 24.

TABLE 24.—SURFACE TENSION OF PURE LIQUIDS

(Measured in dynes per centimeter at 20° by the capillary rise method.)

Water	72.62	Toluene	28.58
Benzol	28.88	Isobutyl alcohol	22.85
Methyl alcohol	22.61	Ethyl butyrate	24.54
Ethyl alcohol	22.27		

Surface Tension and Drop Weight.—Under proper conditions the weight of a drop which will just remain suspended from the end of a glass tip may be used to determine the surface tension of a liquid. It is shown[2] in Table 25 that the weight of the falling drop is proportional to the surface tension for a given dropping tip. On the other hand, the simple theory which equates the

TABLE 25.—COMPARISON OF SURFACE TENSION AND DROP WEIGHTS FOR A GIVEN CAPILLARY TIP

Substance	Temperature	Surface tension = γ	Milligrams per drop = m	$\frac{m}{\gamma}$
Ether	20°	16.80	21.4	1.27
Chlorbenzene	20°	32.10	41.4	1.30
Water	20°	70.60	89.1	1.26
Benzene	22.5°	29.38	35.2	1.21
Ethyl iodide	19.1°	30.00	36.1	1.20
Benzaldehyde	15.4°	39.19	49.8	1.27
Aniline	17.5°	44.10	52.9	1.21
Quinoline	15.4°	45.13	57.0	1.26

[1] Equation (1) above is true only in case the angle of contact between glass and the liquid film is zero. For a detailed discussion of the methods of measuring this angle see A. FERGUSON, "Fifth Report on Colloid Chemistry," British Association for Advancement of Science, 1–13 (1923).

[2] MORGAN, *J. Am. Chem. Soc.*, **30,** 1055 (1908); **33,** 657 (1911); **35,** 1249, 1505, 1750 (1913).

weight of a suspended drop to the total surface tension, $mg = 2\pi r\gamma$, does not lead to a correct value for the actual surface tension. In this equation m is the mass of the *pendent* drop, determined by weighing a drop which falls, r is the radius of the tip, g the acceleration of gravity, and γ the surface tension. This equation would not be true unless *all* of the drop falls, and this is ordinarily very far from the truth. However, a correction for the residual fraction of the drop may be applied,[1] and when this is done, measurements of surface tension by the drop method are in agreement with those based upon capillary rise.

The fraction of the *ideal* drop whose mass should be used to calculate the correct surface tension from the equation given above depends upon a function of the radius of the tip and the diameter of the *falling* drop; that is, m_i (ideal) $= m \times f(r/V^{1/3})$. In Fig. 12 the fraction of the ideal drop which falls is plotted against $(r/V^{1/3})$. Once the volume of the actual falling drop has been determined by experiment, the ratio of the tip radius to the cube root of its volume is calculated; and then the fraction by which the volume of the actual drop must be divided to give the volume of the ideal drop is read from the curve. Then from the known density of the dropping liquid its mass is calculated. This mass when substituted in the equation

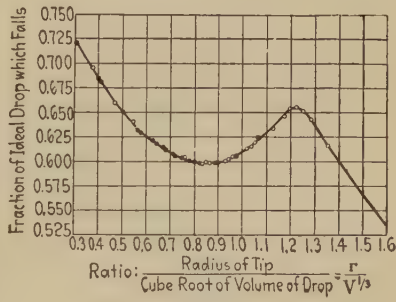

FIG. 12.

$$\gamma = m_i g/2\pi r$$

gives the correct surface tension. In order to emphasize more fully the imaginary character of the ideal drop whose mass is m_i, it is better to write this surface tension equation in the form

$$mg = 2\pi r\gamma f(r/V^{1/3}),$$

where m is the mass of the *actual* falling drop determined

[1] HARKINS, *J. Am. Chem. Soc.*, **38**, 228–253, 354–364, 514–596 (1917); **41**, 449 (1919); compare LOHNSTEIN, *Z. physik. Chem.*, **84**, 410 (1913) for a criticism of the method.

by experiment. An application of the equation to experimental data will serve to illustrate the usefulness of the equation. The mass of a drop of benzene which falls from a tip of radius 0.3926 cm. is 0.0450 gram at 20°. The volume of this drop is 0.0450/ 0.879 = 0.0512 c.c. and the cube root of this volume is 0.371, whence $r/V^{1/3}$ is 1.057. We enter Fig. 12 at the bottom on 1.057 and read at the left that 62 per cent of the ideal drop falls. The weight of the ideal drop is, therefore, 0.050/0.62 = 0.0726, and upon substituting this value for m_i the surface tension γ is 28.80 dynes. As will be seen from Table 24, the surface tension as determined by the capillary rise method is 28.88 dynes.

The drop-weight method has the advantage of employing a much larger liquid surface than the capillary method. When suitable precautions are taken in the experiments and when the drop volumes or drop weights are properly used in the calculations, the method gives results which are comparable in precision with those derived from capillary rise. The details of manipulation allow of less latitude than has commonly been supposed;[1] for example, drops should not fall faster than one in 5 min., and a tip diameter should be chosen such that $(r/V^{1/3})$ is about 0.7 to 1.0.

This method is also adapted to the determination of interfacial tensions, *i.e.*, of the tension in a liquid-liquid interface. A knowledge of this tension (and of the liquid-solid interfacial tension) is a first condition for the quantitative study of many problems in colloid chemistry.

Much research work has been done upon *drop volumes*, in which it has usually been assumed that drop volumes (uncorrected for $f[r/V^{1/3}]$) vary directly with interfacial tensions. Many of the data obtained in this way are not only valueless, but positively misleading.[2]

Surface Tension and Temperature.—The empirical equation of Ramsay and Shields shows the change of molecular surface energy with temperature, where the molecular surface energy is proportional to the product of surface tension and the molecular volume to the $\frac{2}{3}$ power. The equation is

$$\gamma(Mv)^{2/3} = k(t_c - t - d) = k(\tau - d), \qquad (2)$$

[1] HARKINS and BROWN, *J. Am. Chem. Soc.*, **41**, 499 (1919).

[2] See A. FERGUSON, "Fifth Report on Colloid Chemistry," 11 (1923).

where t_c is the critical temperature, t is the temperature at which γ is measured, and τ is the difference between the critical temperature and the temperature of experiment. The quantity $(Mv)^{2/3}$ is proportional to the surface exposed by a mol of liquid; it changes only slightly with the temperature. From the equation it is seen that the surface tension γ decreases as the critical temperature is approached, and that it becomes zero when $(t_c - t)$ is equal to d. The quantity d is a correction factor of 6°, introduced into the equation to show that γ becomes zero at 6° below the critical temperature, in place of at the critical temperature as might be expected. The value of k in the equation is obtained from measurements of γ at different temperatures for one substance; it has the same value for all normal substances. As is also the case with other equations to be given in this chapter, this equation fails to hold for certain liquids which are in some way abnormal; these substances are said to be associated into double and more complex molecules in the liquid state. But for liquids which consist of single non-associated molecules, this equation describes the change of surface tension with temperature in a satisfactory manner. As liquid and vapor do not become identical until the critical temperature is reached, it is difficult to understand why the "correction" term of 6° appears in the Ramsay equation, but if critical temperatures are calculated from the temperature change of surface tension, or from drop weight which is proportional to it, without using this correction term, they are uniformly 6° too low. Critical temperatures calculated with the use of this factor are in surprising agreement with those obtained by direct measurement. In Table 26 are shown some calculations based on drop-weight measurements at two temperatures. The Ramsay equation written as a drop-weight equation is

$$m_i(Mv)^{2/3} = K(t_c - t - 6),$$

where m_i is the weight of an ideal drop, and the other terms have the same meaning as before. Critical temperatures for quinoline and pyridine have not yet been measured, but it will be seen that the value of K derived from measurements at different temperatures is the same as for the other substances, which is evidence that their calculated critical temperatures are probably as correct as the others in this table.

TABLE 26.—CRITICAL TEMPERATURES CALCULATED FROM DROP WEIGHTS AT DIFFERENT TEMPERATURES[1]

Substance	Milligrams Weight per drop at		$m_i(Mv)^{2/3}$ at		K	t_c Calculated	t_c Experiment
	18°	60°	18°	60°			
Benzene	30.96	25.10	614.99	516.44	2.326	288	288
Quinoline	48.10	43.09	1,156.42	1,057.23	2.329	520	
CCl_4	28.85	23.55	607.14	512.89	2.332	285	283
C_6H_5Cl	35.87	30.48	780.31	682.00	2.328	360	359
Pyridine	40.37	34.14	751.71	654.35	2.330	347	

Vapor Pressure.—The pressure at which a liquid and its vapor are in equilibrium at a definite temperature is called the vapor pressure of the liquid. When not in contact with its liquid phase, a vapor may exist at any pressure lower than its vapor pressure. If the volume of such a vapor is gradually decreased at some temperature below its critical temperature, the pressure increases until the vapor pressure is reached. Any further decrease in volume does not increase the pressure, but causes the formation of a liquid phase. As the volume is still further decreased, the pressure remains constant until all of the vapor has condensed to liquid; after which the pressure may be increased to any desired extent. There is only one pressure for a given temperature at which the liquid phase and the gaseous phase may exist in equilibrium, but either phase may exist alone over a considerable range of pressures for any given temperature. It should be clearly understood that a vapor pressure is an *equilibrium* pressure. The partial pressure of water vapor in the absence of liquid may be anything less than its vapor pressure and remain indefinitely so, but its vapor pressure is a saturation pressure at which vapor and liquid will remain indefinitely at equilibrium. The humidity of air, for example, is the ratio of the partial pressure of water vapor in it to the saturation pressure of water at the temperature in question. The pressure of water vapor and the vapor pressure of water are identical only when the humidity is unity.

Vapor Pressure and Temperature.—The vapor pressures of all liquids increase rapidly as the temperature is increased. This

[1] MORGAN and THOMSSEN, *J. Am. Chem. Soc.*, **33**, 657 (1911).

may be seen in the data for water, Table 27, for ammonia, Table 28, and from the curves in Fig. 13.

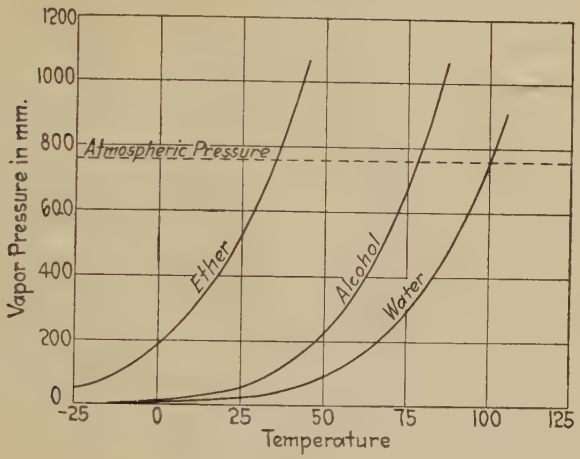

FIG. 13.

TABLE 27.—VAPOR PRESSURE OF WATER,[1] IN MILLIMETERS OF MERCURY

Temperature	Vapor pressure	Temperature	Vapor pressure
−15	1.445	60	149.19
−10	2.160	70	233.53
−5	3.171	80	355.1
0	4.579	90	525.8
5	6.543	100	760.0
10	9.210	110	1,074.5
15	12.794	120	1,488.9
20	17.539	130	2,025.6
25	23.763	140	2,709.5
30	31.834	150	3,568.7
35	42.188	160	4,633.
40	55.341	170	5,937.
45	71.90	180	7,514.
50	92.54	190	9,404.
55	117.85	200	11,647.

[1] *Ann. Physik*, **26**, 833 (1908); **29**, 723 (1909); **31**, 715, 945 (1910).

TABLE 28.—VAPOR PRESSURE OF AMMONIA,[1] IN MILLIMETERS OF MERCURY

Temperature	Vapor pressure	Temperature	Vapor pressure
−80°	37.6	0°	3,221
−70°	81.9	10°	4,612
−60°	164.2	20°	6,428
−50°	306.6	30°	8,749
−40°	538.3	40°	11,658
−30°	896.7	50°	15,245
−20°	1426.8	60°	19,606
−10°	2181.4	70°	24,842

The rate at which the vapor pressure of a liquid changes with the absolute temperature is shown by the following exact equation, called the Clausius-Clapeyron equation, and based on thermodynamics alone.[2]

$$\frac{dp}{dT} = \frac{\Delta H}{(V_g - V_l)T} = \frac{\Delta H}{T\Delta v}. \qquad (3)$$

[1] CRAGHOE, MEYERS, and TAYLOR, *J. Am. Chem. Soc.*, **42**, 228 (1920).

[2] The second law of thermodynamics states that the work done by a reversible cyclical process operating between T and $T + dT$ is

$$dw = q\frac{dT}{T},$$

where q is the heat evolved by the part of the cycle occurring at T. Let the cycle consist of the following steps: (*a*) evaporate a gram of water at T, and under its vapor pressure p, whereby the work done is $p(v_2 - v_1)$; (*b*) heat the vapor to $T + dT$, and allow the pressure to change to $p + dp$ and the volume to $v_2 + dv_2$, doing the work $(p + dp)dv_2$, or pdv_2 if the second-order quantity is neglected; (*c*) condense the vapor to liquid under its vapor pressure $(p + dp)$, doing the work $(p + dp)[(v_1 + dv_1) - (v_2 + dv_2)]$; (*d*) cool the liquid to T, doing the work $-pdv_1$. The sum of all of these quantities of work (neglecting second-order differentials) is $-dp(v_2 - v_1)$ and the heat given to the surroundings at T is $-\Delta H$, since the latent heat ΔH is *absorbed* in step (*a*). Substituting in the second-law equation, we find

$$-dp(v_2 - v_1) = -\Delta H\frac{dT}{T};$$

or

$$\frac{dp}{dT} = \frac{\Delta H}{T\Delta v}$$

This equation can be applied to calculate the effect of pressure on the temperature of any change in state of aggregation, or the effect of temperature upon the pressure of any such change. ΔH is the heat absorbed and Δv is the increase in volume which accompanies the change. Since

In this equation ΔH is the quantity of heat absorbed in vaporizing V_l c.c. of liquid to form V_g c.c. of vapor at the temperature T, and dp/dT is the rate at which the vapor pressure increases with the temperature. Δv is therefore, the increase in volume attending evaporation.

For approximate calculations involving evaporation at pressures not much greater than 1 atmosphere, this equation can be much simplified by neglecting the volume of liquid V_l in comparison with that of the vapor V_g (which is over a thousand times the liquid volume), and by expressing V_g with the aid of the ideal gas law $pV_g = RT$ for one mol of vapor formed. The equation then becomes

$$\frac{dp}{dT} = \frac{\Delta H_m p}{RT^2}, \tag{4}$$

where ΔH_m is now the molal heat of evaporation, since one mol of vapor is formed, and R is the usual gas constant, expressed as 1.99 cal. when the molal latent heat of evaporation ΔH_m is so expressed. Over small ranges of temperature the latent heat is practically constant, and with this assumption the equation may be integrated between limits in order to facilitate calculating the vapor pressure at one temperature from that at some other temperature. The integrated expression is[1]

$$2.303 \log \frac{p_2}{p_1} = \frac{\Delta H_m}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right). \tag{5}$$

As the pressures involved appear as a ratio, p_2/p_1, they may be expressed in any units desired; similarly, ΔH_m and R appear as a ratio and must be expressed in the same units, commonly calories. We may illustrate the use of the equation by calculating the molal latent heat of vaporization of ether from two values of

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the heat effect and the increase in volume are both proportional to the quantity of material involved, the equation may be applied to any quantity of substance. If the pressure is in atmospheres and the volume change is in cubic centimeters, ΔH must be expressed as cubic centimeter-atmospheres; 1 cal. is 41.2 c.c.-atmospheres.

[1] In this book the abbreviation log signifies logarithms to the base 10, that is, ordinary logarithms; natural logarithms, to the base $e = 2.7183$, are abbreviated ln. Then $\ln x = 2.303 \log x$.

its vapor pressure, 534 mm. at 25° and 760 mm. at 35°. Upon substituting in equation (5) we have

$$2.3 \log \frac{760}{534} = \frac{\Delta H_m}{1.99}\left[\frac{1}{298} - \frac{1}{308}\right],$$

whence $\Delta H_m = 6480$ cal. The experimentally determined latent heat is 6260. This is about the concordance to be expected from the approximate equation.

Another approximate equation for the vapor pressure of a substance in terms of its critical temperature and pressure is due to van der Waals. The equation is

$$\log \frac{p_c}{p} = c\left(\frac{T_c}{T} - 1\right), \tag{6}$$

where p_c and T_c are the critical pressure and temperature (page 81), and p is the vapor pressure at the temperature T. The constant c is usually taken as 3, but is smaller for monatomic gases and the halogens, and greater than 3 for some substances.[1]

Boiling Point.—The boiling point of a liquid is the temperature at which its vapor pressure is 760 mm. of mercury, or 1 atmosphere. The temperature at which a liquid is observed to boil in the laboratory under atmospheric pressure is a variable quantity depending upon the location of the laboratory and the existing barometric pressure. It is often necessary to apply a correction to such observed boiling points in order to reduce them to standard boiling points. This correction is usually smaller than a degree, but in places of high altitude it may be very much larger; failure to make such corrections in reporting boiling points has led to small errors in recorded data. It is partly for this reason that the melting point of an organic substance (which is not appreciably affected by moderate changes of pressure) is a better guide to its purity than the boiling point.

The rise in boiling point of a pure liquid per millimeter increase in external pressure is roughly the same fractional amount of the absolute-scale boiling point for all substances, about 0.0001. To compute a true boiling point from one observed at some pressure higher than 760 mm. multiply the excess pressure over 760 mm. by 0.0001 of the absolute boiling point, and subtract this product from the observed boiling point, *i.e.*, subtract $\Delta t = 0.0001T \times \Delta p$. For example, under 772-mm. pressure

[1] Herz, *Z. Elektrochem.*, **25**, 408 (1919).

water boils at $373 \times 0.0001 \times 12 = 0.45°$ higher than at 1 atmosphere, according to the rule just given; the difference in boiling point for 12 mm. pressure found by experiment is 0.44°. When the barometric pressures are below atmospheric pressure, the corrections should, of course, be added to the observed boiling points. For pressures far removed from atmospheric, this simple rule will not give the proper correction. Thus at 525 mm. pressure the boiling point of water calculated according to this rule is 92.2°; the experimental boiling point under this pressure is 90.0°. When it is desired to calculate boiling points at pressures considerably removed from 1 atmosphere, the approximate form of the Clausius-Clapeyron equation (5) will give results of reasonable accuracy; thus in the case just considered, by substituting 9700 cal. for ΔH_m, 1.99 cal. for R, 373 and 760 for T_2 and p_2, 525 for p_1, and solving for T_1, we find $T_1 = 364.0$, whence t is 91°. This will illustrate the divergence to be expected from the use of these two approximate rules. The error in the latter calculation is not due to any fault in the Clausius-Clapeyron equation, which is absolutely exact, but is a result of simplifying it by means of assumptions which are only approximately correct.

Critical Conditions.—As was mentioned at the beginning of the chapter, there is for each substance a **critical temperature** above which it cannot exist as a liquid. At any temperature below this critical one a substance becomes liquid when the applied pressure is greater than the vapor pressure of the substance at that temperature. But at temperatures higher than the critical the liquid phase does not appear, no matter how great the pressure. The **critical pressure** is the pressure which causes the liquid phase to form at the critical temperature. It is thus the last point on the vapor-pressure curve. The **critical density** is the density of the liquid and of the vapor also at the critical temperature and pressure; since under these conditions the liquid phase and the vapor phase are identical in all properties. The **critical volume** is the volume of a gram of substance under the critical temperature and pressure.

Numerical data relating to the critical properties of substances, together with other data to be used in this chapter, will be found in Table 29.

TABLE 29.—BOILING POINTS, LATENT HEATS, AND CRITICAL DATA[1]

Substance	Molal weight (1)	Absolute boiling point (2)	Absolute critical temperature (3)	Molal heat of vaporization (4)	Critical pressure, atmospheres (5)	Critical density (6)	Molal latent heat (Trouton) (7)	Molal latent heat (Herz) (8)	$\frac{d_{crit}}{d_{theor}}$ (9)	$\frac{T_{crit}}{T_{Bpt}}$ (10)
Helium	4.00	4.25	5.25	.....	2.26	0.060	86.3	100	2.8	1.23
Argon	39.9	87	156	.....	48.	0.509	1,765	2,520	3.4	1.79
Krypton	82.92	121	210	.....	54.3	.....	2,450	.....	....	1.73
Xenon	130.2	164	288	.....	57.	1.15	3,330	4,300	3.66	1.75
Hydrogen	2.0	20.5	38.5	.....	13.4	0.0257	416	620	3.39	1.88
Oxygen	32.00	90.1	155	1,600	49.30	0.430	1,830	2,460	3.46	1.70
Nitrogen	28.0	77.3	128	1,330	33.65	0.311	1,570	.....	....	1.64
Chlorine	70.92	240	414	2,390	79.6	.....	4,870	.....	....	1.72
Nitric oxide	30.0	123	179.5	.....	71.2	.....	2,500	.....	....	1.45
HCl	36.5	190	324	3,600	81.5	0.41	3,860	4,820	3.68	1.70
HBr	80.93	204	363	3,940	84.4	.....	4,160	.....	....	1.79
CO	28.0	83	135 3	1,430	34.60	0.3110	1,680	2,070	3.56	1.63
CO_2	44.0	194.7	304	.....	72.85	0.448	3,950	4,750	3.49	1.57
N_2O	44.0	183.2	309.5	4,400	71.65	0.454	3,720	4,400	3.65	1 69
Methane	16.0	108.3	190.15	.....	54.6	0.1623	2,200	3,000	3.47	1.77
Ethane	30.1	190	305.1	3,800	48.85	.....	3,850	.....	....	1.60
Ethylene	28.0	168	282.5	3,510	50.65	.....	3,410	.....	....	1.68
Acetylene	26.0	189.5	308.5	5,150	61.65	.....	3,850	.. ..	....	....
Cyanogen	52.1	252	401.3	5,360	59.75	.....	5,120	.....	....	1.58
Sulfur dioxide	64.0	263	430.1	6,150	77.65	0.513	5,350	6,400	3.64	1.63
Ammonia	17.0	239	406	5,500	112 3	0.2362	4,850	5,380	4.21	1.69
Water	18.0	373	647	9,700	217.5	0.40	7,570	6,500	4.97	1.72
Hydrogen sulfide	34.0	213	373.4	4,500	89.05	.....	4,340	.....	....	1.75
CCl_4	153.8	350	556	7,200	45.	0.56	7,100	7,800	3.68	1.59
$SnCl_4$	260.5	387	592	7,950	37.	0.742	7,860	8,660	3.73	1.53
Methyl alcohol	32.1	338	519	8,420	78.6	0.272	6,870	6,260	4.58	1.53

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
Ethyl alcohol	46.1	351	516	9,960	63.	0.276	7,130	7,000	4.00	1.47
Propyl alcohol	60.1	370	537	.....	50.	0.273	7,500	7,300	4.00	1.45
Ether	74.1	307.6	467.5	6,260	35.6	0.263	6,140	6,620	3.82	1.52
Formic acid	46.0	374	.....	5,550	.....	.....	7,600	.....	....	....
Acetic acid	60.	391	594	5,650	57.2	0.351	7,830	6,540	4.99	1.52
Methyl formate	60.	305	487	6,840	59.5	0.350	6,200	6,720	3.92	1.60
Methyl acetate	74.1	334	507	7,300	46.5	0.327	6,800	6,900	3.94	1.52
Methyl propionate	88.1	356	530	7,660	39.5	0.313	7,240	7,420	3.91	1.49
Methyl butyrate	102.1	375	554	7,900	34.3	0.300	7,620	7,800	3.90	1.48
Methyl *iso* butyrate	102.1	365	541	7,770	34.	0.301	7,320	7,700	3.87	1.48
Ethyl formate	74.1	331	508	7,340	46.7	0.324	6,730	6,910	3.89	1.54
Ethyl acetate	88.1	350	523	7,600	38.	0.308	7,110	7,260	3.95	1.50
Ethyl butyrate	116.1	394	566	8,550	30.2	0.276	8,000	8,850	3.65	1.43
n-Pentane	72.1	309	470	6,070	33.	0.230	6,280	6,780	3.76	1.52
n-Hexane	86.1	343	508	6,820	29.6	0.234	7,000	7,320	3.83	1.48
n-Heptane	100.2	371	540	7,400	27.2	0.234	7,550	7,900	3.85	1.46
n-Octane	114.2	399	569	8,150	24.6	0.233	8,100	8,500	3.86	1.42
iso Pentane	72.1	303	461	5,900	33.	0.234	6,150	6,900	3.73	1.52
Benzene	78.1	353	561	7,450	48.	0.305	7,180	7,700	3.76	1.59
Fluorbenzene	96.1	358	560	7,620	44.6	0.354	7,280	8,100	3.80	1.56
Chlorbenzene	112.5	405	632	8,440	44.6	0.366	8,230	8,800	3.78	1.56
Brombenzene	157.	429	670	8,750	44.6	0.485	8,700	9,250	3.81	1.56
Iodobenzene	204.	461	721	9,440	44.6	0.581	9,350	10,400	3.78	1.56

[1] YOUNG *Proc. Roy. Soc. Dublin*, **12,** 374, (1910); VAN LAAR, *Chem. Weekblad*, **16,** 1557 (1919); CARDOSO, *J. chim. phys.*, **10,** 470 (1912); **13,** 312 (1915); WALDEN, *Z. physik, Chem.*, **65,** 257 (1909).

Many equations of an empirical nature have been proposed to show the relation between critical constants and other properties of substances, but they are not applicable to all substances, and there seems to be no simple rule for determining whether a chosen equation will describe the behavior of a substance or not. Nearly all writers consider a substance as "normal" in its behavior when it conforms to some particular equation, but substances which are normal according to one equation are often abnormal when judged by some other equation. Some of these equations are here given; when actual data are lacking, they are useful in estimating a rough value of critical constants.

It has been known for some time (law of Guldberg-Guye) that the critical temperature of a substance was about three-halves its boiling point, each on the absolute scale. That is $T_c/T_b = 1.5$ for many substances. The values of this ratio are given in column 10 of Table 29, where the maximum variations are seen to be 1.42 to 1.88, except in the case of helium. The validity of the Guldberg-Guye law is doubtful in some cases.[1]

Prud'homme[2] gives another curious relation for which no theoretical basis has yet been discovered; that the sum of the absolute melting point and absolute boiling point is equal to the absolute critical temperature

$$T_{m.p.} + T_{b.p.} = T_c.$$

Young[3] states that the critical density is about 3.7 times the theoretical density of the vapor as calculated from the ideal gas law $pv_m = RT$. Some substances deviate from this rule quite widely—water, acetic acid, methyl alcohol, and ammonia are examples (see column 9 of Table 29). These substances also do not conform to the simple rules relating to heat of evaporation and are for other reasons considered to be abnormal. Their abnormality probably consists in a more or less close chemical combination of the molecules into double and larger aggregates; at least such a combination offers a ready explanation of the deviations. These will be considered more fully at the end of the chapter but they should be kept in mind while the various rules are under discussion.

[1] Moles, *J. chim. phys.*, **17**, 415 (1919).
[2] *J. chim. phys.*, **21**, 243 (1924).
[3] *Proc. Roy. Soc. Dublin*, **12**, 374 (1910).

Law of Average Densities.—As the temperature is raised, the density of saturated vapor increases rapidly, owing to the increase of vapor pressure of the liquid. The density of the liquid phase decreases as the temperature is raised; at first slowly, then more rapidly as the critical temperature is approached. At the critical temperature the density of liquid becomes the same as that of the saturated vapor; there is, therefore, in this region considerable difficulty in distinguishing the separate phases, and

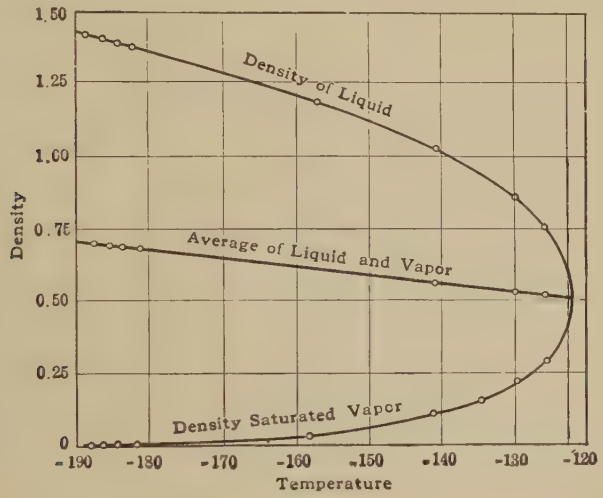


FIG. 14.

an exact determination of the critical density is difficult. It has been found that, as the critical temperature is approached, the average of the density of the liquid and its saturated vapor is a linear function of the temperature. This statement will be clearer from an examination of Fig. 14, which shows the density of liquid argon and its coexisting saturated vapor.[1] By plotting this average density against the temperature and drawing a straight line through the points it is easy to determine the point at which this line intersects the curve showing the density of each phase, and thus to read the critical density. This statement is known as the law of Cailletet and Mathias,[2] after its dis-

[1] KAMMERLINGH ONNES and MATHIAS, *Comm. Phys. Lab. Univ. Leiden*, **117** (1911).

[2] *Compt. rend.*, **102**, 1202 (1886).

coverers, or as the law of rectilinear diameters, since the diameter of the density curve is a straight line.

Latent Heat of Evaporation.—Energy is required to overcome the attractive forces acting between the molecules of a liquid; and hence in separating them during evaporation a considerable quantity of heat is required. This heat added to a boiling liquid does not raise the temperature of it or of its vapor, but it is used in the expansion which takes place when a liquid changes to a vapor. If the evaporation takes place into a vacuum, all of the heat is used in separating the molecules of the substance. When the evaporation takes place against the atmosphere, as is usually the case, a certain volume of the air must be pushed back to allow space for the vapor formed. This work is also done at the expense of heat absorbed during the evaporation; hence evaporation at atmospheric pressure requires more heat than evaporation into a vacuum. The volume of a mol of vapor is about RT (that is, 82 T) c.c. when the pressure is 1 atmosphere, and this volume of air must be displaced by the vapor formed. If the difference is desired in calories, R has the value 1.99; in cubic-centimeter-atmosphere units R is 82.

The quantity of heat required per molecular weight of vapor formed from its liquid is called the molecular heat of vaporization, or the molal latent heat. Its value is roughly the same for all liquids of the same boiling point; it is larger for liquids of high boiling point and smaller for those of low boiling point. This fact is expressed in the so-called **Trouton's rule,** which states that the molal latent heat of evaporation in calories is about 20 times the boiling point, on the absolute scale, when the evaporation takes place under 1 atmosphere pressure. This is expressed by the equation

$$\frac{\Delta H_m}{T_b} = 20.6 \qquad (7)$$

When evaporation takes place at a higher pressure than 1 atmosphere, and hence at a higher temperature, smaller latent heats are observed. This decrease continues until at the critical point no heat is required to evaporate the liquid.

Trouton's rule, like many empirical laws, is an approximation of considerable usefulness when rough data are desired; but

it is not strictly exact. The deviations are shown in Table 29, in which the figures of column 7 should be the same as those of column 4 if there were no deviations of the rule. In homologous series of compounds the value of the Trouton constant increases somewhat as the boiling point of the liquid increases.

Many modifications of Trouton's rule have been suggested from time to time; most of which bring some classes of substances into better agreement than is obtained with the simple Trouton rule. Nernst proposes

$$\frac{\Delta H_m}{T_b} = 9.5 \log T_b - 0.007 T_b. \qquad (8)$$

Hildebrand[1] suggests that a better value of $\Delta H_m/T$ is obtained when the evaporation takes place at such a temperature that equal concentrations of vapor are obtained.

In estimating molal latent heats where no data exist, the simple Trouton rule will probably be found as satisfactory as any of its modifications, since the latter are not reliable in every case, and there is no simple rule for determining whether the liquid in question is a "normal" substance or not.

Herz[2] gives a relation between the latent heat of evaporation and the critical temperature, critical pressure, and critical density, based on the fact that the product $Mp_c/T_c d_c$ has the same numerical value as the Trouton constant, $\Delta H_m/T_b$, where M is the molecular weight, T_b the boiling point, and the other terms refer to the critical data. By substituting for T_c its approximate equivalent $1.5T_b$ (Guldberg-Guye law) and equating the two terms given above, the equation

$$\Delta H_m = \frac{2Mp_c}{3d_c} \qquad (9)$$

is obtained. The latent heats so calculated are shown in Table 29, column 8. They should be compared with those derived from Trouton's rule, and with those derived from direct experiment.

Viscosity.—By the viscosity, or internal friction, of a liquid is meant its resistance to flow, which is a measure of the friction between the liquid layers as they slide over one another through a

[1] *J. Am. Chem. Soc.*, **37,** 970 (1915).
[2] *Z. Elektrochem.*, **25,** 321 (1919).

pipe or tube. The absolute unit of viscosity is the force in dynes which is necessary to move a square centimeter of liquid surface with unit velocity past a stationary liquid surface 1 cm. away from it. Measurements are made by flowing the liquid through a small tube of known dimensions under a measured pressure, or from the oscillations of a disc suspended in the liquid. It is necessary in making such measurements that the flow of liquid be parallel to the sides of the tube, and not turbulent in character, since the resistance to turbulent flow is greater than the resistance to "stream-line" flow. This means only that the tube must be quite small for liquids of low viscosity.

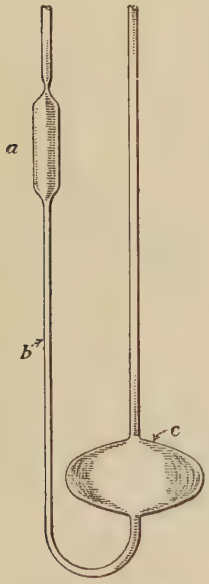


FIG. 16.—Washburn type of viscosimeter.

The viscosity of a liquid relative to that of water at the same temperature is more commonly measured, and is called "relative viscosity."

One type of instrument[1] for measuring relative viscosity is shown in Fig. 16. It consists of a bulb a for measuring the quantity of liquid flowing, a capillary tube b, and a receiving vessel c. By applying pressure to the tube above c, the liquid is forced into the upper bulb until it stands somewhat above the upper mark, the pressure is then released, and time is measured while the meniscus passes from the mark above the bulb a to a mark below this bulb. As the driving force is a column of the liquid itself, this force varies with the density of the liquid, and it is necessary to multiply the time of flow by the density in making a comparison. Thus denoting by η the viscosity, D the density, and t the time of flow of an unknown liquid through a given viscosimeter, and by η_w, D_w, and t_w the corresponding quantities for water, the relative viscosity of the unknown liquid (referred to that of water as unity) is given by the expression

$$\frac{\eta}{\eta_w} = \frac{Dt}{D_w t_w}. \qquad (10)$$

[1] WASHBURN and WILLIAMS, *J. Am. Chem. Soc.*, **35**, 737 (1913).

Relative viscosities obtained in this way may be changed to those in terms of the absolute system by multiplying the numbers so obtained by the viscosity of water at the temperature in question. These values are as follows:

TABLE 30.—VISCOSITY OF WATER[1] AT ATMOSPHERIC PRESSURE

t	η	η_t/η_0
0	0.01793	1.0000
10	0.01310	0.7300
18	0.01057	0.5898
25	0.00893	0.4974
40	0.00657	0.3668
50	0.00550	0.3064
75	0.00380	0.2120
100	0.00284	0.1584

Liquids increase their viscosity considerably when under pressure, especially at low temperatures, and the increase for a given unit of pressure is greater at higher pressures.[2] All liquids decrease in viscosity at higher temperatures, the decrease for water near room temperature being about 2 per cent for each degree rise in temperature. (It should be noted that gases *increase* in viscosity at higher temperatures, as on account of the increased number of collisions the molecules interfere with each other to a greater extent.)

Arrhenius has found an empirical relation between the change of viscosity and the temperature of a pure liquid, as follows:[3]

$$\frac{d \log \eta}{dT} = \frac{K_1}{T^2 V^{1/3}}, \tag{11}$$

where V is the volume of a gram of liquid of viscosity η, and K_1 is a constant, which for a given liquid is proportional to its

[1] HOSKING, *Proc. Roy. Soc. N. S. Wales*, **43**, 37 (1909).

[2] BRIDGMAN, *Proc. Nat. Acad. Sci.*, **11**, 603 (1925) gives data at 30° and 75° for pressures up to 12,000 kg. per square centimeter. Water at low temperatures and low pressures decreases its viscosity with rising pressure, but above 25° it behaves as do other liquids. Above 1000 kg. per square centimeter the increase of viscosity with pressure is very rapid.

[3] ARRHENIUS, *Meddel. Vetenskapsakad. Nobelinst.*, **3**, 20 (1918); THORPE, *Science Progress*, **12**, 583 (1918).

boiling point on the absolute scale, as shown in the following table. The value of the quotient K_1/T_b for homologous series of compounds increases slightly with the boiling point, in the same way as does the constant of Trouton's rule.

For computing the viscosity of a liquid at one temperature from that at another temperature, the above equation is more useful in the integrated form:

$$(V^{\frac{1}{3}}) \log \left(\frac{\eta_1}{\eta_2}\right) = K_1 \left(\frac{1}{T_1} - \frac{1}{T_2}\right). \qquad (12)$$

K_1 may be obtained from Table 31.

TABLE 31.—VISCOSITIES AND ARRHENIUS' CONSTANTS

Substance	$10^5 \eta V^{\frac{1}{3}}$	$\frac{K_1}{T_b}$
Unsaturated hydrocarbons	233	1.002
Acetaldehyde	249	1.005
Paraffins	257	1.078
Ketones	270	1.074
Mercaptans	275	1.012
Iodides	277	1.073
Acid anhydrides	279	1.153
Esters	288	1.169
Monochlorides	296	1.129
Thiophene	341	1.243
Carbon tetrachloride	400	1.452
Water	290	1.800
Formic acid	507	1.800
Acetic acid	398	1.387
Propionic, butyric acids	342	1.322
Methyl alcohol	380	1.562
Allyl alcohol	483	2.507
Other primary alcohols	422	2.087
Secondary alcohols	552	3.066
Tertiary alcohols	579	3.784

The substances below the dotted line are believed to be associated into larger molecules in the liquid state, and hence give a large value of the coefficient K_1/T_b.

Certain substances (shown below the dotted line in Table 31) do not seem to conform to this rule; they are, for the most part,

the substances which did not follow Trouton's rule, and which for other reasons are considered abnormal. But the relation between K_1 and the boiling point holds for such a variety of chemically unrelated substances as to indicate that the nature and constitution of the molecule are only subordinate in producing internal friction.

Viscosities of Mixtures.—The problem of expressing the viscosity of a mixture of liquids in terms of the properties of the pure substances is still an unsettled one. Egner[1] states that the expression

$$\log \eta = x_1 \log \eta_1 + x_2 \log \eta_2$$

holds for mixtures, where x_1 and x_2 are the mol fractions of the two liquids; η_1 and η_2 are their viscosities. Kendall[2] states that the viscosities of mixtures are not any simple function of the per cent by weight, of the mol fraction, or of volume concentration, but he finds that for certain mixtures the formula above leads to results for mixtures which are only slightly lower than measured viscosities. Bingham proposes that the best representation of viscosities in mixtures is

$$\frac{1}{\eta} = \frac{a}{\eta_1} + \frac{b}{\eta_2},$$

where a and b are the volume concentrations of the liquids present.

Molecular Association in the Liquid State.—In the preceding paragraphs mention has been made of "abnormal" substances, that is, substances which did not follow some particular rule, often an empirical one. These deviations are believed to indicate that in the liquid state the molecules are more or less strongly combined into double or triple molecules, held together by forces somewhat different from primary valence forces, and of a less specific character. There is evidence of such "association" into larger molecules or groups of molecules, derived from abnormalities in boiling points or vapor pressures, from volume changes on mixing liquids, from deviations from the rectilinear diameters of Cailletet and Mathias, from the compressibility of

[1] *Meddel. Vetenskapsakad. Nobelinst.*, **3**, 22 (1918).

[2] *J. Am. Chem. Soc.*, **39**, 1787 (1917); KENDALL and WRIGHT, *J. Am. Chem. Soc.*, **42**, 1776 (1920); KENDALL and MONROE, *J. Am. Chem. Soc.*, **43**, 115 (1921).

water, from the critical constants, from surface tension and from viscosity measurements.

When attempts are made to compute the extent of this association, whole numbers are seldom obtained, which indicates that the combination is never complete and that these numbers are averages. And when the degrees of complexity as determined by rival methods are compared, such wide discrepancies are observed that one questions whether any known method of measuring this association is reliable. In the appended table are shown the values of the association factor for a few substances by various methods. Thus Tyrer computes that water in the liquid state is $(H_2O)_{6.3}$ while Longinescu writes $(H_2O)_{4.6}$ and Bingham $(H_2O)_{2.2}$. The futility of quantitative discussion of this data is evident, but it should be said that most of the methods agree as to *which* liquids are considerably associated and which ones have nearly the normal molecular weight corresponding to the formula as usually written. The case of water has been studied more than that of any other liquid; the "association factor" is not found to be a whole number by any of the methods. Most authorities seem to agree that liquid water is largely a mixture of $(H_2O)_2$ and $(H_2O)_3$ in proportions which vary with the temperature.[1] There are also simple $(H_2O)_1$ molecules present, and these evaporate to give water vapor, which has nearly the normal molecular weight.

Table 32 shows the number of simple molecules combined into a complex liquid molecule according to various authorities.

Quite a different point of view is taken by Langmuir,[2] who assumes that the molecules of liquids are held together in the liquid state by chemical forces which are of the same character as the forces acting between atoms. This is the "residual valence" which is sometimes used to describe the purely chemical forces such as those holding solvate or hydrate water to molecules in solution. Langmuir considers that the entire body of a liquid is a single molecule and that there is no such thing as a molecular weight in the liquid state.

[1] A full discussion of the case of water will be found in *Trans. Faraday Soc.*, **6**, 71–123 (1910); the whole subject has been treated by W. E. S. Turner in a monograph in the Findlay series of textbooks.

[2] *J. Am. Chem. Soc.*, **38**, 2221 (1916).

TABLE 32.—EXTENT OF MOLECULAR ASSOCIATION IN THE LIQUID STATE

Substance	Tyrer I[1]	Tyrer II	Ramsay and Shields[2]	Longinescu[3]	Batchinski[4]	Bingham[5]	Walden[6]	From volume relations[7]
Water	6.30	1170	1.64 to 2.32	4.6	2.13 to 1.10	2.20	2.66 to 1.41	5.60
Acetic acid	2.00	2.02	2.77	1.7	2.74	1.73	1.8—2.8	4.74
Formic acid	2.70	....	3.13	1.8	2.68	....	3	
Methyl alcohol	2.55	3.51	3.24 to 2.20	3.2	3.43	1.79	2.2—3.2	3.81
Ethyl alcohol	1.89	2.90	2.43	2.1	3.65	1.74	2.0—3.2	5.37
Acetone	....	1.13	1 26	...	2.74	1.23	1.2—1.5	....

[1] *J. Phys. Chem.*, **19**, 81 (1915).
[2] From surface-tension measurements.
[3] *J. chim. phys.* **6**, 552 (1908).
[4] From critical constants.
[5] *Am. Chem. J.*, **43**, 287 (1910).
[6] *Z. physik. Chem.*, **65**, 257 (1908).
[7] *Z. physik. Chem.*, **80**, 50 (1912).

Arrangement of Molecules in Liquid Surfaces.—Marcelin[1] found that when a liquid insoluble fatty acid is placed upon water, it spreads rapidly over the surface until a certain definite area is reached, after which it does not tend to spread further. The spreading has been studied thoroughly by Langmuir,[2] and later by Adam,[3] both of whom measured the area covered by very small quantities of fatty acids of known composition. A weighed quantity of fatty acid of high molecular weight, and insoluble in water, was dissolved in a large quantity of benzene; a weighed drop of this dilute solution was placed on the water surface. The benzene soon evaporated and left a quantity of fatty acid far smaller than it would be possible to weigh directly, but of accurately known weight. The floating film was pressed against the end of a rectangular tray containing the water on which it was floating, and its area was carefully measured. Many experiments showed that the area was directly proportional to the quantity of fatty acid, demonstrating that the spreading took place only to a certain definite limit in every case.

[1] *Ann. Physik*, **1**, 19 (1914).
[2] *J. Am. Chem. Soc.*, **39**, 1848 (1917); *Proc. Nat. Acad. Sci.*, **3**, 251 (1917).
[3] *Proc. Roy. Soc. London*, (*A*) **99**, 336 (1921).

The explanation of the limited spreading is as follows: There is no great attraction of the water for the fatty acid molecules as a whole, as this would manifest itself as a solubility of the fatty acid *in* the water, whereas it remains *on* the water and does not enter the water phase as a whole. The acids consist of two parts, the —COOH group and an oily hydrocarbon chain. Now the —COOH group is attracted by water, as shown by the solubility of the lower organic acids in water, and as would be expected since the group would then find itself in a medium containing hydroxyl groups such as it contains. But the fatty part is, like all hydrocarbons, only slightly soluble in water and but little attracted by water. Langmuir states that when oleic acid, for example, is placed upon water, the carboxyl groups do *actually dissolve in the water*, that is, they combine with it by secondary valence forces, and the fatty chain remaining outside of the water. By spreading as a *monomolecular* layer, all of the carboxyl groups enter the water without causing the hydrocarbon chains to separate from one another. Further spreading, however, would bring water molecules into the surface between the hydrocarbon chains and separate them. The attraction of the hydrocarbon part for molecules of its own kind prevents this and the spreading ceases.

From the weight of fatty acid employed, its molecular weight, and Avogadro's number, the number of molecules in a film of known area was readily calculated, and from this the cross-section of a single molecule was calculated. It will be seen from Table 33 that the area is the same for all of the acids having a single hydrocarbon chain. The case of tristearin indicates that the $C_3H_5\equiv$ group has dissolved in the water layer, or at least is turned toward the water, leaving three hydrocarbon chains in the oil surface, since the area per molecule is three times that of a single chain. On account of the double bond in oleic acid, this substance appears to be bent double in its chain, and triolein occupies six times the surface of a single chain. The fact that the area per molecule for the first three acids in the table is the same indicates that the chains are standing on end and projecting into the oil layer, and that the carboxyl group is dissolved in the water layer. The square root of this molecular area thus gives the diameter of the hydrocarbon chain, which is of the same order of magnitude as the molecular diameters calculated on page 64.

Since the thickness of the oil film is the length of the hydrocarbon chain, it is easy to calculate the length of chain per carbon atom; this also is seen to be of the order of 10^{-8} cm., similar to the diameters calculated for small gaseous molecules.

TABLE 33.—MOLECULAR DIMENSIONS CALCULATED FROM THE SPREADING OF OIL FILMS ON WATER

Substance	Molecular cross-section Sq. Cm.	Molecular Diameter = $\sqrt{\text{Cross-Sec.}}$ Cm.	Length of Molecule = thickness of oil film	Length per Carbon atom in the Chain
Palmitic acid, $C_{15}H_{31}COOH$	21×10^{-16}	4.6×10^{-8}	24.0×10^{-8}	1.5×10^{-8}
Stearic acid, $C_{17}H_{35}COOH$	22	4.7	25.0	1.39
Cerotic acid, $C_{25}H_{51}COOH$	25	5.0	31.0	1.20
Tristearin $(C_{18}H_{35}O_2)_3C_3H_5$	66	8.1	25.0	1.32
Oleic acid, $C_{17}H_{33}COOH$	46	6.8	11.2	0.62
Triolein $(C_{18}H_{33}O_2)_3C_3H_5$	126	11.2	13.0	0.69
Myricyl alcohol, $C_{30}H_{61}OH$	27	5.2	41.0	1.37

Similar views as to the structure of surfaces have been developed independently by Harkins[1] from a study of the decrease in free surface energy which takes place when two liquid surfaces are brought together. The active groups, such as —COOH, =CO, —CN, —OH, or $—CONH_2$, strive to enter the water. If the hydrocarbon chain attached to such a group is not too large, it can be dragged into water by the active group, and the compound will be soluble in water to a greater or less extent, depending upon the quantity of insoluble hydrocarbon chain in the molecule. If the hydrocarbon tail is too large, it cannot be brought into the water by the attraction exerted on the active group, and two liquid phases result. The active ends still enter the water, however, and give rise to the surface structure already explained.

When a liquid is in contact with its vapor, the molecules in the surface layer probably arrange themselves so that the least active portion of the molecule is toward the vapor phase. At any interface between phases the molecules probably arrange themselves so that the passage from one phase to the other will be as little abrupt as possible. That is, the hydrocarbon part of a molecule adsorbed in the interface between water and an oil-like substance will be turned toward the oil layer. It is this molec-

[1] *J. Am. Chem. Soc.*, **39**, 354, 541 (1917).

ular orientation which sets up at the surfaces of liquids and solids the so-called electric double layer. The stability of emulsoid particles also seems to depend upon this surface arrangement; the best emulsifying agents are long-chain compounds with a highly active group on one end of the molecule, such as soaps. These matters are discussed further in Chapter XV.

Questions

1. The heat of vaporization of water at its boiling point is 538 cal. per gram. Calculate the vapor pressure of water at 80°, and the percentage error of the calculated pressure. Refer to Table 27 for the measured vapor pressure at 80°.

2. The vapor pressure of benzene is 548 mm. at 70° and 755 mm. at 80°. (*a*) Calculate the quantity of heat required to vaporize a gram of benzene. (*b*) Calculate the vapor pressure of benzene at 90°. *Ans.* 99 cal., 1030 mm.

3. Calculate the value of Trouton's constant, $\Delta H_m/T$ for several typical liquids in Table 29, and tabulate them. What is a possible explanation of the variations in the case of liquids whose constants are over 20? What liquids show the largest deviations from Trouton's rule? What types of liquids conform to it most closely?

4. Calculate the molal latent heat of vaporization for water, benzol, ammonia, and oxygen by means of the modifications of Trouton's rule, and compare the errors of these calculations with those from the simple Trouton rule. Refer to Table 29 for the data.

5. The viscosity of water at 25° is 0.00893. Calculate its viscosity at 100° by the integrated Arrhenius equation, using the data of Table 31. The measured value is 0.00284.

6. Calculate from the simple gas law the density of acetic acid at its critical temperature and pressure, 321° and 57 atmospheres. Apply Young's ratio to determine whether acetic acid is associated in the liquid state.

7. Calculate the vapor pressure of alcohol at 90°, using the data given in Table 29.

8. Calculate the area which would be covered by a milligram of oleic acid ($C_{17}H_{33}COOH$) when allowed to spread upon a water surface.

9. The densities of liquid ammonia and saturated ammonia vapor are as follows:

Temperature	Liquid Density	Vapor Density
98.75	0.4640	0.0533
109.25	0.4339	0.0691
116.4	0.4056	0.0873
121.3	0.3831	0.1024
123.2	0.3750	0.1085
125.45	0.3584	0.1220
129.6	0.3246	0.1509

Plot the density of each phase against the temperature, and determine from this plot the critical temperature and critical density of ammonia, using the law of rectilinear diameters. (A. Berthoud, *Helvetica Chim. Acta*, **1**, 84 (1918).)

10. Benzol has a surface tension of 28.88 dynes at 20° and its density is 0.879. What is the diameter of a capillary tube in which benzene rises 1 cm.? How high would water rise in the same tube?

11. The vapor pressure of bromine is 200 mm. at 23.5° and 400 mm. at 40.5°. Calculate the latent heat of evaporation of a gram of bromine.

12. The boiling point of ethyl alcohol is 78.4° when its pressure is 1 atmosphere. The heat of vaporization is 9960 cal. per mol. Calculate the boiling point of ethyl alcohol under a pressure of 100 mm.

13. Ethyl ether absorbs 93 cal. per gram when it evaporates at 0°C. and its vapor pressure at this temperature is 186.1 mm. Calculate the vapor pressure at −25°. The observed pressure at this temperature is 50 mm.

14. The vapor pressure of copper is 209 mm. at 2175° and 300 mm. at 2215°. Calculate the latent heat of evaporation for copper and the Trouton constant.

15. The capillary rise has been determined for propane in a capillary tube of radius 0.0276 cm. at a series of temperatures. From the stated values of the temperature, capillary rise, and density, determine the surface tension at each of the temperatures and show that the plot of γ against temperature is a straight line.

t	h	d
−71.0	2.39	0.6155
−66.1	2.32	0.6099
−63.5	2.29	0.6069
−53.7	2.13	0.5958
−46.1	2.02	0.5871
−39.1	1.94	0.5790

(Maas and Wright, *J. Am. Chem. Soc.*, **43**, 1108 (1921).)

16. Drop-weight experiments were made at 20° for water and for benzene with the following results:

Tip Radius, Cm.	Drop Weight for Water (Grams)	Drop Weight for Benzene (Grams)
0.1477	0.0469	0.0175
0.2680	0.0775	0.0297
0.3419	0.0964	0.0383

Calculate from these drop weights the surface tension of benzene and of water at 20°, and compare them with the measured results given in Table 24. (Harkins and Brown, *J. Am. Chem. Soc.*, **41**, 449 (1919).)

CHAPTER IV

SOLID SUBSTANCES

The most important characteristics of the solid state are rigidity, and a definite arrangement of the atoms or molecules of a crystal with reference to one another. It has long been known that the forces acting between constituent atoms of solid substances were specific in character, and of great magnitude. In general, there is no tendency for a substance in crystallizing from its melt or from solution to include the molecules of other substances; and this affords a ready means of purification of the products of chemical operations. Certain chemically related substances have the property of forming mixed crystals; in these cases recrystallization is not a suitable method of purification, and other means suited to the problem in hand must be employed.

The changes in properties attending the passage of a substance from liquid to solid are much smaller than those which attend the condensation of a gas. The density of a solid is commonly within 10 per cent of that of its liquid, while the density of a liquid is often a thousand times that of the vapor from which it was formed. Solids have vapor pressures, just as liquids have; they increase with increasing temperature as in the case of liquids. The rate at which the vapor pressure, or sublimation pressure, changes with temperature may be calculated from the Clausius-Clapeyron equation; but since the change in state is from solid to vapor, the heat term is the sublimation heat of the solid. The equation is

$$\frac{dp}{dT} = \frac{\Delta H_s}{T\Delta v},$$

where ΔH_s is the molecular latent heat of sublimation, and Δv is the increase in volume upon sublimation. If the volume of the solid is neglected and that of a mol of vapor is assumed to

be RT/p, an approximate form of this equation suited to rough calculations is

$$\frac{dp}{dT} = \frac{p\Delta H_s}{RT^2}.$$

The **melting point** of a substance is that temperature at which its liquid and solid phases are in equilibrium under a pressure of 1 atmosphere. As the presence of some other substance lowers the melting point in proportion to the quantity of it present, an accurate determination of melting point is a ready means of establishing the purity of a product.

Changes of pressure have but slight effect upon the melting point of a solid, except where very high pressures are involved. For example, an increase of 2100 atmospheres lowers the melting point of ice 22°. The effect of pressure on the *melting point* can also be calculated from the Clausius-Clapeyron equation,

$$\frac{dp}{dT} = \frac{\Delta H_f}{T\Delta v},$$

where Δv is the increase of volume which takes place on melting, and ΔH_f is the heat of fusion. Here an approximate form of this equation obtained from the ideal gas law cannot, of course, be applied. If the effect of pressure is desired in degrees per atmosphere, Δv should be expressed in cubic centimeters, and ΔH_f in cubic-centimeter-atmospheres. One calorie is equivalent to 41.2 c.c.-atmospheres. For example, the heat absorbed during the melting of a gram of water is 79 cal., the increase in volume upon melting is -0.09 c.c., whence

$$\frac{dp}{dT} = \frac{79 \times 41.2}{-0.09 \times 273} = -132$$

atmospheres per degree, which corresponds to $1/-132 = -0.0076°$ per atmosphere. The negative sign indicates that pressure lowers the melting point of ice.

By considering the kinetic energy of the molecules of solids, and their energy of vibration, Honda[1] has derived an approximate relation between the heat of fusion and absolute melting point, which is somewhat similar to Trouton's rule for liquids. The rule is restricted to elements alone, and states that the atomic heat of fusion in small calories is two times the absolute

[1] *Phys. Rev.*, **12,** 425 (1918).

melting point. The rule holds roughly for several metals, but is greatly in error for many others, indicating that the true relation between latent heat and melting point has not yet been discovered. Thus the quotient of $\Delta H_f/T$ is 4.8 for bromine and chlorine, 3.3 for tin, 4.7 for bismuth, 3.8 for iodine, etc., but between 1.9 and 2.6 for most metals of high melting point.

Heat Capacity of Solids.—Two simple laws express roughly the heat capacities of substances near room temperature; the first refers to elements, the second to compounds. The law of Dulong and Petit states that the product of specific heat and atomic weight (that is, atomic heat capacity) is about 6.2 cal. per degree for all of the solid elements at constant pressure. Elements of atomic weight less than 40 appear to be exceptions

TABLE 34.—HEAT CAPACITIES OF THE ELEMENTS

Element	Atomic heat at constant volume, C_v	Atomic heat at constant pressure, C_p
Sodium	6.4	6.9
Magnesium	5.8	6.0
Aluminum	5.7	5.8
Potassium	6.5	7.1
Iron	5.9	6.0
Nickel	5.9	6.1
Copper	5.6	5.8
Zinc	5.6	6.0
Palladium	5.9	6.1
Silver	5.8	6.1
Cadmium	5.9	6.2
Tin	6.1	6.4
Antimony	5.9	6.0
Iodine	6.0	6.9
Platinum	5.9	6.1
Gold	5.9	6.2
Thallium	6.1	6.4
Lead	5.9	6.3
Bismuth	6.2	6.3
Average	5.9	6.2

The average deviation of C_v from 5.9 is only half as large as the average deviation from C_p of 6.2.

to the rule. It has been found[1] that the atomic heat capacity at constant volume is more nearly constant for all elements than that at constant pressure, for when the heating is carried out at constant volume there is no work of expansion done against the internal forces which hold a solid together. The average atomic heat capacity at constant volume is 5.9 cal. per degree. A comparison of these two rules is given in Table 34, where all of the data refer to room temperatures. As explained in a later section, all of these heat capacities decrease rapidly at low temperatures, and increase slightly for higher temperatures.

Several elements, notably those of low atomic weight, are exceptions to these rules; they have much smaller atomic heat capacities than heavier elements. For example, some of these atomic heat capacities are sulfur 5.5, phosphorus 5.6, carbon 1.6 (diamond) to 1.9 (graphite), boron 2.5, silicon 4.8, aluminum 5.7.

Kopp's law states that the molecular heat capacity of a solid compound is the sum of the atomic heat capacities of the elements composing it; the elements having atomic heat capacities lower than those required by the law of Dulong and Petit retain these lower values in their compounds. The heat capacity of an atomic weight of oxygen in a solid compound is naturally not the same as that of an atomic weight of gaseous oxygen at the same temperature; but it may be found from the difference between the formal heat capacity of a metal oxide and the heat capacity of the metal contained in it. The average heat capacity of

TABLE 35.—HEAT CAPACITIES AND KOPP'S LAW OF ADDITIVE ATOMIC HEATS

Substance	Molecular heat capacity		Per cent error	Substance	Molecular heat capacity		Per cent error
	Measured	Kopp's law			Measured	Kopp's law	
$PbCl_2$.....	18.50	18.6	0.5	PbI_2.....	19.60	20.1	3
NaCl.....	12.80	13.1	2	PbS.....	12.2	11.70	4
AgCl.....	13.04	12.3	5	KI.....	13.60	14.0	3
TlCl.....	12.60	12.4	2	AgI.....	13.45	13.0	3
$ZnCl_2$.....	18.55	18.4	1	$CaCO_3$...	20.20	20.0	0.5
				SiC.....	6.40	6.6	3

[1] LEWIS, *J. Am. Chem. Soc.*, **29**, 1165 (1907).

oxygen so obtained is 4.0 cal. per degree per atomic weight; the atomic heat capacity of hydrogen in its solid compounds is 2.3 cal. per degree. For example, the molecular heat capacity of carborundum (SiC) is 6.4, that calculated from Kopp's law is 4.8 + 1.8 = 6.6; the measured value for lead sulfide is 12.2, the calculated one 6.2 + 5.5 = 11.7; for sodium chloride the measured value is 12.8, the calculated one 13.1. This illustrates the agreement generally obtained by the application of this law; some further examples are shown in Table 35.

Heat Capacity and Temperature.—When the investigations on heat capacities of solids were extended to low temperatures

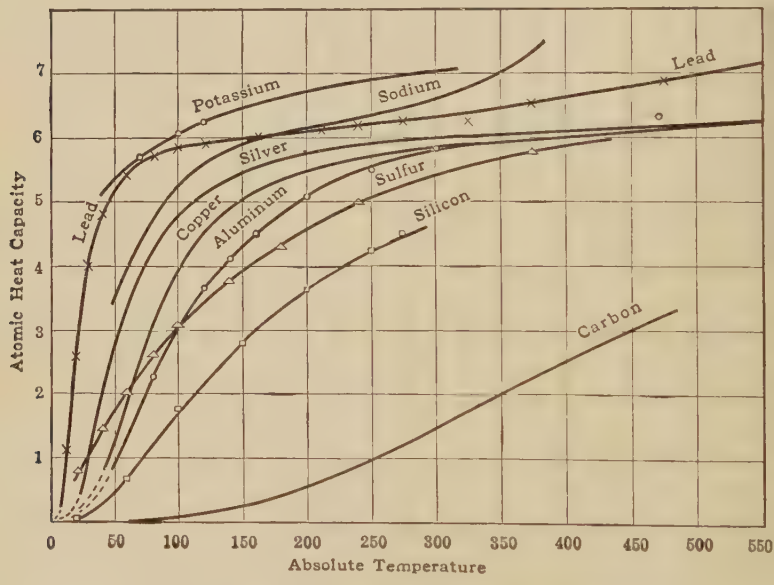


FIG. 17.—Change of atomic heat capacity with temperature.

it was found that the law of Dulong and Petit failed completely and that at the very lowest temperatures the specific heats of all substances became very small and approached zero. Similarly, at higher temperatures many elements showed atomic heat capacities considerably greater than 6.2. Some data on the atomic heats of elements at low temperatures are given in Table 36 and shown in Fig. 17. It will be noted that in the neighbor

hood of 300° absolute, which is about room temperature, most of the elements conform to the law of Dulong and Petit, that is, have atomic heat capacities of about 6 cal. per degree. At lower temperatures this heat capacity decreases much more rapidly for some elements than for others. Thus at 100° absolute, about the temperature of liquid air, potassium and lead still have nearly their normal heat capacities, while those of copper and aluminum have decreased to half of the ordinary values. All of the curves point toward zero heat capacity as the absolute zero of temperature is approached, all of them show at the lowest temperatures a convex curvature toward the temperature axis, followed by a change of curvature at higher temperatures, then a portion which is nearly horizontal. This suggests that the heat capacity of all substances may be expressed by the same form of equation, with a different constant or set of constants for each element.

In connection with the discussion of the heat capacity of gases it was noted that the absorption of heat increased the velocity of the molecules and also increased the energy content of the gas in some other (unexplained) way. This latter energy effect was made evident by the increase in the heat capacity of the gas at a higher temperature. There is certainly no very large motion of the atoms or molecules of a solid in any one direction, but it seems probable that they may vibrate about *mean positions* and that the heat absorbed by a solid is used to increase the intensity of these vibrations. Einstein assumed that all of the atoms of a single solid substance were in vibration at a characteristic frequency, and he derived an equation for the heat capacity of a solid element in terms of this frequency. His equation seemed to be of the right form for showing the change of heat capacity with the temperature, but it was not in very good accord with measured heat capacities. Nernst and Lindemann[1] derived another equation which allowed for two vibration frequencies, the second of which corresponded to a vibration of the atoms with a frequency half that of the characteristic one. The characteristic frequency may be calculated from the melting point of the element, from its compressibility, or from the spectrum of the light reflected from it. The calculations of heat capacity are

[1] *Z. Elektrochem.*, **17**, 817 (1911).

laborious and not always satisfactory, but they do show the general shape of the specific-heat curve.

TABLE 36.—ATOMIC HEAT CAPACITIES OF THE ELEMENTS[1] AT VARIOUS TEMPERATURES

Absolute temperature	Al	C	Cu	Pb	S	K	Si	Ag	Na
20	0.07	0.00	0.11	2.62	0.79	....	0.03	0.39	....
40	0.53	0.00	0.81	4.82	1.46	....	0.25	2.00	....
60	1.43	0.018	1.90	5.43	2.05	....	0.68	3.37	4.01
80	2.30	0.048	2.98	5.73	2.60	....	1.25	4.22	4.77
100	3.01	0.084	3.94	5.86	3.08	6.04	1.78	4.76	5.27
120	3.64	0.144	4.58	5.91	3.45	6.24	....	5.12	5.61
140	4.12	0.222	4.93	5.96	3.77	6.36	2.60	5.37	5.82
160	4.53	0.330	5.15	6.01	4.07	6.48	....	5.55	5.93
180	4.84	0.456	5.30	6.05	4.31	6.60	....	5.67	6.05
200	5.10	0.594	5.43	6.10	4.55	6.70	3.62	5.77	6.14
220	5.29	0.750	5.55	6.15	4.76	6.77	....	5.86	6.26
240	5.45	0.924	5.65	6.20	4.99	6.84	4.14	5.92	6.35
260	5.58	1.116	5.73	6.25	5.19	6.92	....	5.95	6.39
273	5.64	1.236	5.78	6.28	5.24	6.98	4.53	6.00	6.53
298	5.74	1.45	5.83	6.31	5.40	7.04	....	6.02	6.66
323	5.84	1.83	5.88	6.34	....	....	....	6.04	6.85
373	6.04	2.24	5.98	6.51	5.98	....	....	6.08	7.40
473	6.34	3.24	6.14	6.88	....	....	....	6.14	....

A better equation has been derived by Debye,[2] assuming that the atoms vibrate with all frequencies from zero to a certain maximum number. This equation is also very complicated, but for high temperatures it reduces to the simple form $C_v = 3R$, and for very low temperatures it becomes

$$C_v = 77.94 \times 3R \left(\frac{T}{\theta}\right)^3,$$

[1] The data are from the following sources: GRIFFITHS, *Proc. Roy. Soc. London*, (*A*) **90**, 557 (1914); EASTMAN and RODEBUSH, *J. Am. Chem. Soc.*, **41**, 489 (1919); KEESOM and ONNES, *Comm. Phys. Lab. Univ. Leiden*, **147a** (1915); MILLS, *J. Phys. Chem.*, **21**, 359 (1917); SCHÜBEL, *Z. anorg. Chem.*, **87**, 81 (1914).

[2] *Ann. Physik*, **39**, 789 (1913).

where θ is proportional to the maximum vibration frequency. The heat capacity at low temperature is thus proportional to the third power of the absolute temperature; the dotted portions of the curves of Fig. 17 are of the right shape to correspond with this fact.

Much still remains to be done upon the problem of heat capacity, however. Thus the atomic heats of sodium, potassium, and magnesium tend toward much higher values than the $3R$ predicted by Debye's equation,[1] and the elements iron, nickel, cobalt, bismuth, tin, and chromium do not approach $3R$ as an upper limit of their atomic heat capacities,[2] but aluminum, copper, silver, zinc, and cadmium do approach such a limit. No adequate explanation suited to all of these cases has yet been found.

Forces Acting between Atoms.—The great tensile strength and the slight compressibility of metals are incompatible with the older idea that solids are composed of hard particles (molecules) separated by considerable spaces. Richards[3] has studied carefully the changes in volume which accompany the formation of compounds, and from the magnitude of these changes (they were always decreases in volume) he concludes that the atoms themselves are compressed during combination. Now it is known that the pressures required to compress elementary solid substances are enormous; since the chemical reaction produced these compressions, the forces there operating must also be very large. In Table 37 are given the sums of the atomic volumes of

TABLE 37

Substance	Volume of metal plus chlorine	Molal volume of salt formed	Contraction during formation of compound	Part of contraction due to metal	Pressure which would cause same contraction. atm.
Lithium chloride	38.1	20.5	17.6	5.1	43,000
Sodium chloride	48.7	27.2	21.5	9.0	24,000
Potassium chloride	70.4	37.3	33.1	20.6	14,000
Rubidium chloride	80.8	44.0	36.8	24.3	10,500
Caesium chloride	96.0	42.4	53.6	41 1	9,500

[1] LEWIS, *Proc. Nat. Acad. Sci.*, **4**, 25 (1918).

[2] SCHÜBEL, *Z. anorgan. Chem.*, **87**, 89 (1914).

[3] *J. Am. Chem. Soc.*, **36**, 2417 (1914); and earlier papers.

the reacting elements, the volume of a mol of alkali chloride, the decrease in volume accompanying the combination, the part of this decrease due to the compression of the alkali element alone (the compression of an atomic weight of chlorine was 12.5 c.c.), and the pressure in atmospheres which would be required to produce the same change in volume in the alkali element.

This compression is brought about by *chemical* forces, that is, the forces holding the atoms of solids in their positions, and it is seen that these forces are of great magnitude.

Arrangement of Atoms in Crystals.—Before discussing the modern work on this subject, it will be instructive to consider briefly what knowledge preceded this work, and to speculate upon the various possible arrangements which may be expected to agree with this knowledge. It is a familiar fact that the crystals of different substances have different external forms. The crystallographer measures the angles between the faces of a crystal, and he refers the planes forming these faces to imaginary axes placed within the crystal. He finds that the intercepts of these planes, when the axes have been properly chosen, occur at distances from the origin which are to one another as simple whole numbers. The classification of crystals is more simple when their internal symmetry is considered with reference to the proper axes than when the faces are considered. For many crystals the axes are not at 90 deg. to one another, and often the axes are of unequal lengths.[1] Some of the crystal faces may be parallel to one or two of the axes and so have no intercept at all upon them. Thus if we consider the simplest case of equal rectangular axes, a plane which cuts one axis and is parallel to the other two,

[1] All crystals may be classified according to the following systems: (*a*) *cubic*, where the three crystallographic axes of reference are of equal length and at right angles to one another; (*b*) *tetragonal*, where only two axes are equal, but all are at right angles; (*c*) *rhombic*, with three unequal axes at right angles; (*d*) *monoclinic*, with two axes at right angles and all of unequal length; (*e*) *triclinic*, with three oblique unequal axes; (*f*) *hexagonal*, with three axes in a plane intersecting at angles of 60 deg. and a fourth axis through the intersection and perpendicular to the plane; (*g*) *trigonal*, with three axes of equal length, at equal angles other than 90 deg. For a discussion of the development of crystal faces referred to axes in the various systems, reference should be made to texts on crystallography or to any large encyclopedia.

as shaded in the left-hand sketch of Fig. 18, has only one intercept. This is called the 1,0,0 plane, or simply the 100 plane. A plane such as the shaded one shown in the middle sketch of Fig. 18 has two intercepts and is called the 110 plane, and the shaded plane on the right is called the 111 plane. Thus the notation describing a plane gives the reciprocal of the distance from the origin at which it cuts each axis of reference. These numbers are also called the Miller indices.

A substance which crystallizes in the cubic system might develop its 100 faces only and be, in reality, a cube. All of the faces of the cube would be 100 faces with respect to rectangular axes having their origin in the center of the crystal. Another substance crystallizing in the cubic system might develop only

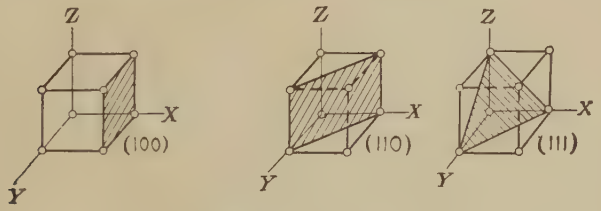


FIG. 18.—Notation of atomic planes.

111 faces (as in one form of magnetite); or it might develop both 100 and 111 faces, as in galena, a sulfide of lead. In the latter two cases the crystal would not be a cube, of course, but it would still be considered as a crystal of the cubic system, for all of its faces may be referred to three equal rectangular axes. The reasons which govern the development of one set of faces in place of another set are entirely unknown.

The constancy of crystal form in a given substance, regardless of the size of the crystals which are developed, suggests that a unit of packing is repeated over and over throughout the crystal corresponding to some systematic arrangement of points in space of three dimensions. In elementary substances the unit might well be a single atom and it is entirely possible that the single atoms (rather than molecules) of compounds might make up the "point" which forms the basis of the "space lattice," as it is called. The repetition of this unit in three-dimensional space

is responsible for the internal arrangement of the atoms or molecules within a crystal.

It is interesting, but not very safe, to speculate upon what arrangement the atoms may take. We have no information whatever as to the shape of an atom or molecule, but in the absence of any information it may be instructive to assume temporarily that atoms are spheres. It does not follow from

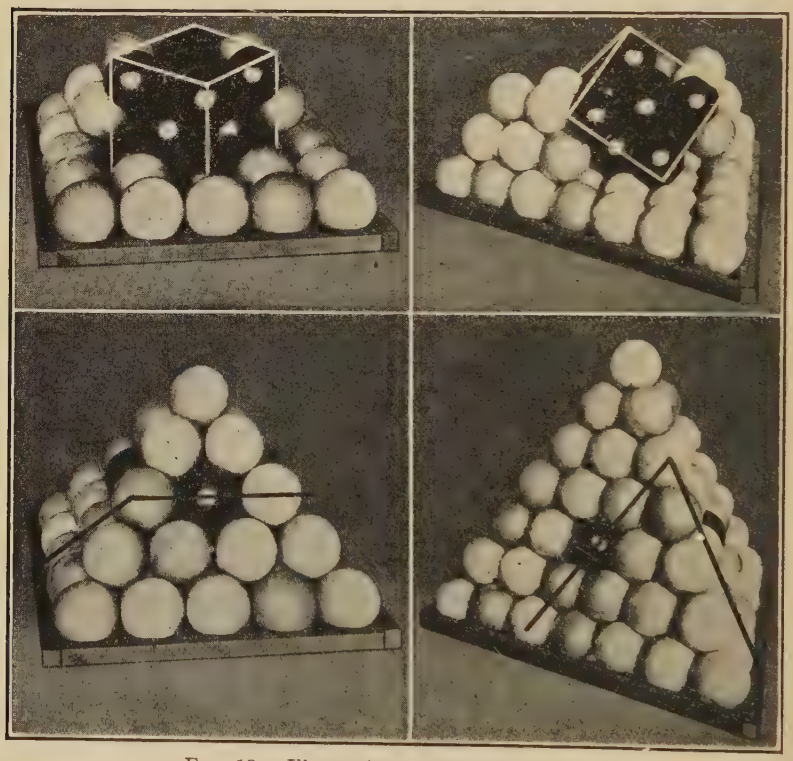


FIG. 19.—Illustrating cubic close packing.

the fact that a substance crystallizes in a cubic system that its atoms are arranged at the corners of imaginary cubes; but since all crystals may be described with reference to axes which are straight lines, and since the natural faces of crystals are planes, it seems proper to assume that the arrangement is one in which the constituent units lie in planes. It seems reasonable to

suppose also that some of these planes, perhaps the most important planes, are parallel to the developed faces of the crystal. For example, in the piles of spheres shown at the bottom of Fig. 19, the external form of the "crystal" is not that of a cube. The arrangement of the "atoms" may be shown to possess cubic symmetry in both of these arrangements, however, by removing some of the spheres and noticing the "unit cube" of black balls. In the pyramid with the square base, shown at the left, the horizontal planes are 100 planes, and in that with the triangular base the horizontal planes are 111 planes. It may be seen that the distance between these horizontal planes is less than the diameter of the spheres. In both cases the spacing of the 110 planes is equal to the diameter of the spheres. These 110 planes are defined by lines drawn over the balls in the pyramids. While the external form of the two piles of spheres appears to be quite different, the arrangement is cubic close packing, and it is the same arrangement in both pyramids. The different external shape results from developing different planes. We shall return to a further consideration of the problem in three dimensions after a brief examination of a simpler one in two dimensions to illustrate the method of attack. But it may be suggested here that a determination of the relative spacings of these planes would give some information regarding the method of packing the atoms in a crystal.

It is a familiar fact that as one rides by an orchard[1] planted in some systematic way the confusion of tree trunks is resolved into straight rows of trees when the orchard is viewed from certain angles. As one rides on, confusion appears to replace regularity until presently at some other angle straight rows are seen again. It is probably a less familiar fact that the distance between the straight rows would be different when viewing the orchard at different angles, but a glance at Fig. 20 will show that this must be so. Now suppose that one is given the distance between these straight rows of trees as viewed from several *distant* points, and that it is required to draw a plan of the orchard from these spacings. A set of such spacings is given in

[1] The author is indebted to Dr. W. P. Davey of the General Electric Company for the illustration of the orchard (see *Gen. Elec. Rev.*, **28**, 586 (1925)).

the first column of Table 38, with the largest distance given first and the others in order of decreasing distance; in the second column the ratio of each of these spacings to the largest one has been obtained by dividing each distance by 17.7 ft.

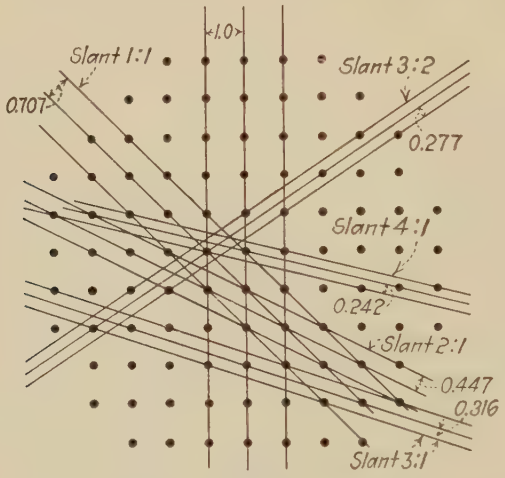


FIG. 20.

TABLE 38.—DISTANCE BETWEEN ROWS IN A SIMPLE SQUARE AND A CENTERED SQUARE

Distance between rows (feet)	Ratio from experiment (17.7 = 1)	Ratio calculated for simple square	Ratio calculated for face-centered square
17.7	1.00	1.00	1.00
12.5	0.71	0.707	0.707
7.9	0.45	0.447	0.477
5.6	0.32	0.316	0.316
3.4	0.19	0.277	0.195
3.0	0.17	0.242	0.171

The next step is to assume some simple plan and see whether the relative distances between straight rows are in agreement with it. Let us assume for a beginning that the orchard is planted with trees at the corners of squares 17.7 ft. on a side and that the angles of view are illustrated in Fig. 20. The third column of Table 38 shows the ratios calculated for this simple

square arrangement for the various angles, and it is obvious at once that some of the ratios correspond to such a plan and others do not. This is, therefore, not the correct plan, for a correct one must correspond to *all* of the ratios observed; but it is probable that a square enters into the plan, since the first four ratios agree with the experimental ones. Now let us assume that the plan of the orchard consists of a tree at each corner of an imaginary square and an additional tree in the center of each square (a centered square such as the "five" face on dice). The spacing of the straight rows of trees as viewed from some of the points of observation would be changed, but it would be unchanged when viewed from some other points, such, for example, as the 1:1 ratio. Furthermore, the largest distance between rows would be less than the side of the assumed square, for a view directly at the side of the square would show a row corresponding to the trees in the centers of the squares. That this set of measurements corresponds to a "face-centered square" of 25 ft. is shown by the figures in the last column of Table 38. Once a method applicable to the spacing of planes of atoms in crystals has been developed, the problem in three dimensions may be attacked in the same way, choosing some simple arrangement as a working basis and discarding it in favor of another as soon as it is found to be incorrect.[1]

Returning now to the piles of spheres shown in Fig. 19, it will be seen from the black spheres that the arrangement is a face-centered cube; that is, that each sphere in the face of the "unit" formed by black spheres is equidistant from four others in the same plane with it. The "crystal," therefore, has the same atomic *plan* as the orchard, if 100 planes are considered.

Application of X-rays to Crystal Structure. The Nature of X-rays.—X-rays are now known to be a form of radiant energy similar to light, apparently possessed of the same velocity, but of much shorter wave lengths. Probably on account of the extremely small wave length, they are able to penetrate matter which is quite opaque to ordinary light. For crystal study, X-rays are usually generated in a "Coolidge tube" by the impact

[1] More general analytical methods have been developed which are applicable to the problem in three-dimensional space. See WYCKOFF, R. W. G., "The Structure of Crystals," Chemical Catalog Company, 1924.

of electrons of high velocity upon a target of molybdenum or tungsten. The electrons are given off by a heated filament, and are driven against the positive electrode or "target" by maintaining the latter at a very high potential. X-rays so generated consist of various wave lengths varying in intensity, and are called "white" X-rays by analogy to "white" light. When the tube is operated at a sufficiently high potential, much more intense X-rays of a single wave length, or of a very few wave lengths, are generated in addition to the general X-radiation. These lines correspond somewhat to the visible line spectrum of incandescent vapors, and are characteristic of the material composing the target. By means of an absorbing screen of not too great thickness or density it is possible to screen out the general or "white" X-radiation, leaving a beam of nearly monochromatic X-rays of great intensity. The wave lengths may be determined in the way outlined in the next section.

Determination of Wave Length.—Attempts to determine the wave length of X-rays by ruled diffraction gratings, such as serve to measure wave lengths of visible light, were without success. Considerations into which we need not enter here made it seem probable that the wave lengths were 10^{-8} or 10^{-9} cm., so that a grating would have to approach atomic spacing in order to diffract X-rays and produce constructive interference at certain angles. The thought at once suggests itself, Can the planes of atoms[1] in a crystal be made to serve as a diffraction grating? The problem might be stated in the following way: If we knew the wave length of some X-ray beam, we might determine atomic spacing, from measurements of the angles at which constructive interference occurred; or if atomic spacing was known, the X-ray wave length could be measured.

The ingenuity of Sir William Bragg[2] and his son evolved a procedure for accomplishing both measurements. Let it be

[1] Laue appears to have been the first to suggest the possibility of employing atomic planes for diffraction gratings. The "Laue photographs" obtained when a beam of general X-radiation is passed through a crystal, and its diffraction is recorded on a photographic plate, lead to the same conclusions regarding the structure of crystals as those given here, but the interpretation of the photographs is more difficult. See *Sitzb. kgl. Bayer. Akad. Wiss.* (1912); *Jahrb. Radioakt. Elektronik*, **11**, 308 (1914).

[2] Bragg, *J. Chem. Soc.* (London), **109**, 252 (1916).

assumed (for the moment the assumption may be called entirely groundless) that the atoms in a cubic crystal such as sodium chloride are arranged at the corners of cubes in space. A formula weight of sodium chloride weighs 58.5 grams, and since the density of this salt is 2.17, the molal volume is 58.5/2.17, or 27.0 c.c. This volume contains 6.0×10^{23} atoms of each element, or 12×10^{23} atoms in all; and they form a cube 3 cm. on a side, or of 27-c.c. volume. The volume available for each atom is $27/(12 \times 10^{23})$ or 22.5×10^{-24} c.c., and the cube whose volume is 22.5×10^{-24} c.c. is 2.81×10^{-8} cm. on an edge. Hence *if the structure of the crystal is a simple cubic lattice*, as assumed, its 100 planes are 2.81×10^{-8} cm. apart.

As stated above, X-rays possess the power of penetrating matter to a remarkable extent. If each atom in the various

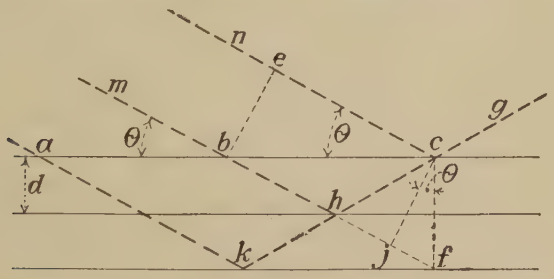


FIG. 21.

planes *within* a crystal acts as a diffraction center, the diffracted wave front builds up in the same way as if reflection had actually occurred, according to Huygen's principle. As the consideration is simpler from the point of view of reflection, we shall treat it in this way, following Sir William Bragg. But it should be kept constantly in mind that it is not a surface reflection with which we are concerned, but diffraction from the atoms composing thousands of parallel planes which lie deep within the crystal.

The parallel dash lines of Fig. 21 represent the advancing wave front of a beam of X-rays of a single wave length λ (as yet unknown), and the horizontal lines correspond to the 100 planes of atoms in a crystal, separated by the distance d (still to be determined). If the beam is striking at such an angle θ that

the "reflected" beam along the line *hcg* is not in phase, destructive interference results, and the intensity of the reflected beam is very low. Only when the angle θ is such that the difference in the paths *ecg*, *mhg*, *akg*, etc., is a *whole number* of wave lengths will the reflections from different planes reinforce one another and give rise to an intense reflected beam, for the apparent reflection of X-rays differs from ordinary reflection of light in that the beam penetrates *into* the crystal and gives rise to reflection from many planes. It will be seen also that unless the planes of atoms are *accurately* spaced at the distance d, destructive interference would take place for all incident angles of the beam, and there would not be any reflected beam of marked intensity. Suppose θ is so chosen that the reflected beam has maximum intensity; the difference in the paths *ecg* and *bhg* is a whole number of wave lengths, $n\lambda$. As *ec* is equal to *bj*, and *hf* is equal to *hc*, the difference in path $bhg - ecg = hc - hj$, and this is equal to $hf - hj$, or *jf*. Now *jf* divided by *cf* is the sine of the angle θ, and *cf* is twice the interplanar distance; then it follows that

$$n\lambda = 2d \sin \theta.$$

There will be some other angle for the reflection when n will have another whole number value, but the number of such reflections is limited. The reflections when n has the value 1, 2, 3, etc. are called first-, second-, and third-order reflections; they become successively fainter as the value of n increases, and necessarily cease when $n\lambda$ approaches $2d$.

From this relation, assuming d to be known for sodium chloride, the wave length of X-rays was obtained by Bragg.[1] By considering the angles of reflection corresponding to constructive interference of the various orders, a value of the wave length of a *single* wave may thus be established.

There is still the *assumption* of a cubic arrangement which remains to be justified. This may be accomplished by an application of the orchard illustration to a space lattice in three dimensions, for if the lattice is really cubic, the relative spacings of the 100, 110, and 111 planes will be to one another as $1 : \sqrt{2} : \sqrt{3}$.

[1] *J. Chem. Soc.* (London), **109**, 252 (1916). For a detailed account of the extensive work done by Professor Bragg and his son, reference should be made to their excellent book, "X-rays and Crystal Structure," Harcourt and Brace (1925).

$1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}}$

And the *relative* spacings may be measured in terms of the angles of constructive interference for X-rays of a *constant* wave length even if the actual wave length is unknown. From such reasoning Professor Bragg and his son established the fact that rock salt crystals are simple cubic in structure, with the atoms forming the corners of the cubes as shown in Fig. 22.

The cubic nature of a rock salt crystal being established from the relative spacing of the planes, there is at hand a set of planes, uniformly spaced 2.81×10^{-8} cm., and these may serve as a diffraction grating for penetrating X-rays which at a measured angle θ produce constructive interference of a maximum intensity. From the equation $n\lambda = 2d \sin \theta$, it was thus determined that

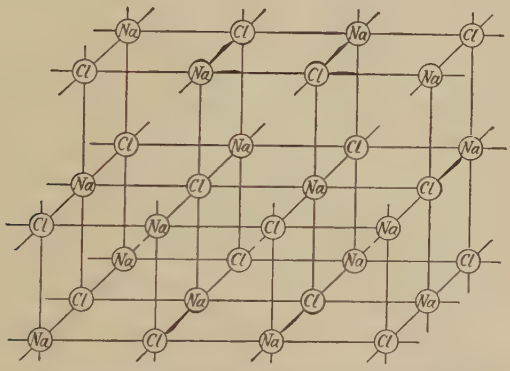


FIG. 22.—Arrangement of atoms in a crystal of sodium chloride.

X-rays generated at a molybdenum target were peculiarly intense in radiation of wave length 0.712×10^{-8} cm. This particular line is known as the K_α line for molybdenum. Other metals when made to serve as targets for electrons give similarly a few lines of characteristic wave length and high intensity.

X-ray Spectrometer.—In order to determine the angle at which constructive interference occurs, a single large crystal may be mounted in the path of the X-ray beam on a turntable (Fig. 23) carrying a chamber filled with methyl bromide vapor, and to which an electroscope is connected. The reflected X-ray beam ionizes the gas to an extent dependent upon its intensity, and thus the rate at which the electroscope leaf falls measures

the intensity of the beam corresponding to the angle at which the crystal face is set to the X-ray beam. By plotting the angle against the intensity, the angles corresponding to maximum for reflections of the 1, 2, 3, etc. order are readily determined. Since this angle is 2θ, the plane spacing follows at once from the relation $n\lambda = 2d \sin \theta$.

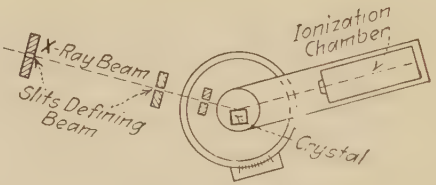


FIG. 23.—Diagram of an X-ray spectrometer.

Method of Rotating Crystal.—Instead of the tedious method of seeking with an ionization chamber the angle of maximum intensity of reflection, the crystal may be rotated in the X-ray beam about one of its principal axes, and the constructively reinforced beam which occurs for an instant whenever the crystal comes into the proper position for any order of reflection may be recorded by prolonged exposure on a photographic film.

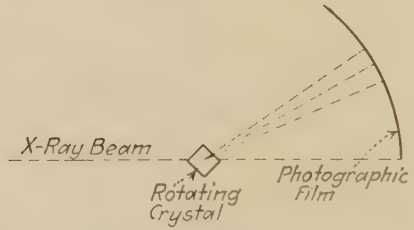


FIG. 24.—Arrangement for rotating-crystal method.

The arrangement is shown in Fig. 24. Since the film is bent on the arc of a circle of known radius and of which the crystal is the center, the angles corresponding to the various orders are proportional to the linear distance of the dark lines on the film from the lower edge. Their sines are proportional to the distances between planes, and thus we obtain data similar to that used in planning the "orchard" above.

Powder Method.[1]—In a finely powdered crystalline material the particles are arranged at random, and in a sufficiently large quantity of powder some particles would be set at the proper angle for reflections of every order for every set of planes. When such a powder is put in place of the rotating crystal of Fig. 24, a "powder pattern" is obtained on the film. This would contain all the lines obtainable by rotating the crystal successively about all of its axes of symmetry. Thus there is obtained an arrangement of lines on the film which is characteristic of the substance. In Fig. 27 the powder patterns are shown for copper and nickel. These metals have the same arrangement of atoms, both are in the face-centered cube, and their patterns are exactly similar, but with different distances between groups of lines corresponding to the different atomic volumes of the elements.

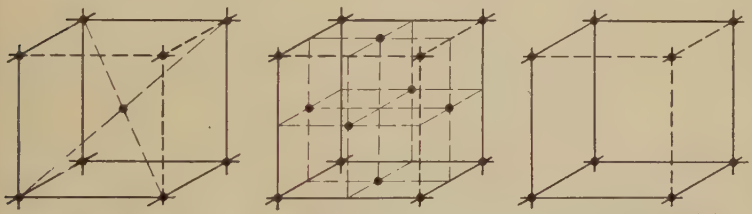


FIG. 25.

Types of Unit Cell.—For substances whose atoms are arranged in cubic symmetry, the three common types of "unit cell" are the simple cube, face-centered cube, and body-centered cube, shown in Fig. 25. The types of arrangement of atoms in crystals are much better appreciated by observing the actual arrangement of spheres packed in the various ways. There should be provided a number of uniform spheres and a box with glass sides or a frame in which to pack them. Three-dimensional models similar to the sketch of Fig. 22 are also very helpful, but their construction is laborious. If only a single unit cube is constructed, it

[1] This method was developed independently by A. W. HULL, *J. Am. Chem. Soc.*, **41**, 1168 (1919) and by DEBYE and SCHERRER, *Nachr. Kgl. Ges. Wiss. Göttingen*, **17**, 277 (1916).

should be made clear that its repetition in space is as indicated at the left of Fig. 26 and not that shown on the right.

The arrangement of the atoms in space has already been worked out for hundreds of crystalline substances and the number is being increased rapidly by many investigators who have taken up this line of work.[1] Sodium bromide, potassium chloride, potassium bromide, and magnesium oxide, among other substances, have structures in which the atoms are arranged in a simple cubic lattice like that of sodium chloride shown in Fig. 22. It is not safe to generalize from these facts that all salts of the KCl type have the simple cubic arrangement, however. For example, cuprous chloride and cesium chloride conform to the body-centered cubic arrangement.

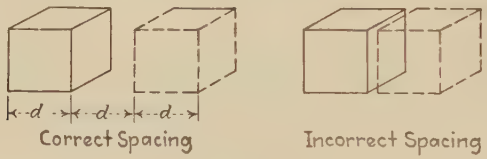


FIG. 26.

Arrangement of Atoms in Metals.—The powder method of X-ray analysis has been used to determine the arrangement of atoms in the metals[2] and other substances which usually cannot be prepared in large single crystals suitable for measurement by the single-crystal method. The most common arrangement of atoms in metallic crystals is the face-centered cubic, which is obtained by dividing the space in a crystal into closely packed cubes and placing an atom at each cube corner and at the center of each cube face (see Fig. 25). This arrangement is also called cubic close packing, and is one of the two alternative arrangements that hard spheres of equal size assume when closely

[1] An excellent book, "X-rays and Crystal Structure," Harcourt and Brace (1924), describing the work on this subject has been written by Professor Bragg and his son, in which will be found details of the analysis of crystalline structure. Another excellent book is "The Structure of Crystals," by R. W. G. WYCKOFF, Chemical Catalog Company (1924). Photographs of atom models will be found in *Nature*, **105**, 646 (1920); see also BRAGG, *Science Progress*, **15**, 367 (1921).

[2] HULL, *Proc. Am. Inst. Elec. Eng.*, **38**, 1171 (1919); *Science*, **52**, 227 (1920).

packed by pressure and shaking. Aluminum, nickel, copper, rhodium, silver, platinum, gold, and lead have this arrangement of atoms in their crystals. The second type of arrangement in metals is the cube-centered arrangement, with an atom at each cube corner and at the center of each elementary cube. The atoms so arranged are not so closely packed as in the face-centered cubic arrangement, and this arrangement is not stable for spheres, which indicates either that the atoms of these elements are not spheres or that they are held in position by special types of forces. Lithium, sodium, chromium, iron, molybdenum, and tungsten conform to this second type. The third common type of arrangement for metals is obtained by dividing the space into equal closely packed, right-triangular prisms, the bases of which are equilateral triangles, and the altitudes 1.633 times the side of the triangles. An atom is located at each prism corner and at half of the prism centers. This is the second alternative arrangement assumed by equal spheres under pressure and shaking, and is the form shown by magnesium,[1] zinc, and cadmium. The simple cubic arrangement is not shown by metals, but is confined to salts with equal numbers of positive and negative atoms, such as the alkali halides and magnesium oxide. The tetrahedral arrangement, in which each atom is surrounded by four others arranged in a regular tetrahedron, is found in the diamond, carborundum, silicon, and in ammonium chloride.

The powder patterns enable one to distinguish readily the nature of the unit cell which is close packed in a metal. In Fig. 27 the upper film[2] compares the powder pattern for iron, which is a body-centered cube unit, with copper, which is a face-centered cube unit, and it is evident at once that the patterns are entirely different for these two types. In the lower part of Fig. 27 the powder patterns for copper and nickel are compared. Both patterns consist of two lines, then one line after a space, then two lines again, etc. The actual spacings are somewhat different on account of the different atomic volumes of copper and nickel, but from the general similarity in arrangement it is obvious that these two metals have the same space lattice.

[1] *Proc. Nat. Acad. Sci.*, **3**, 470 (1917).

[2] The author is indebted to Prof. J. T. Norton for preparing these powder patterns.

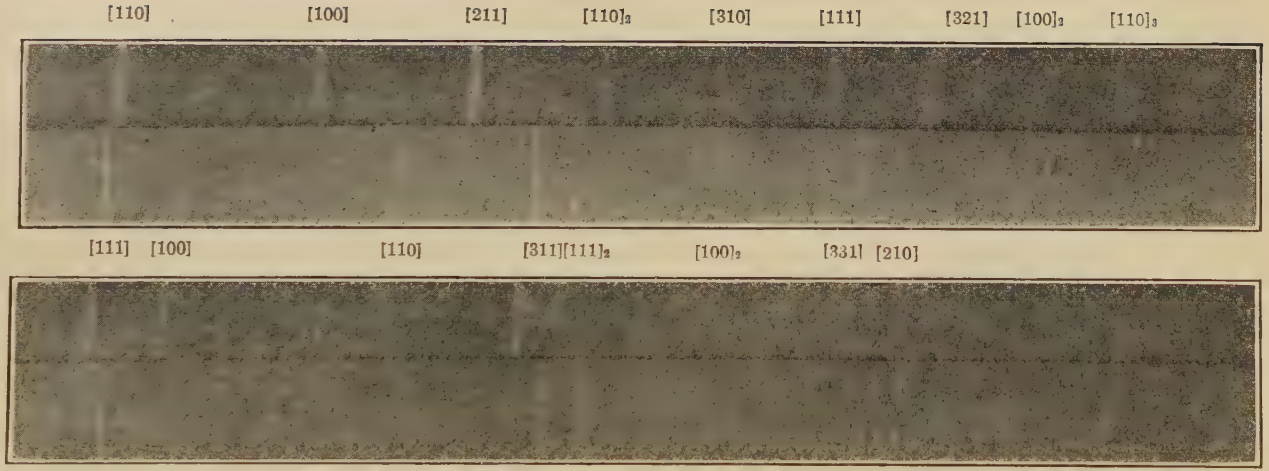
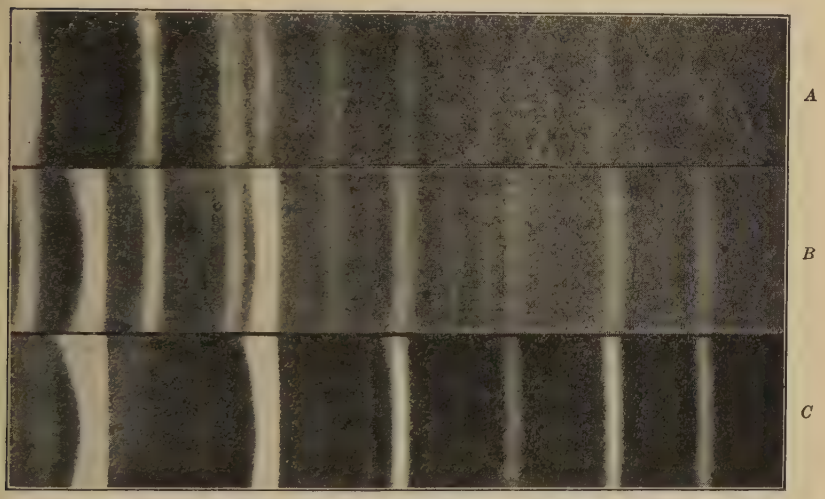


FIG. 27.—Upper strip, comparison of powder pattern for body-centered iron and face-centered copper. Lower strip, face-centered copper and face-centered nickel. The numbers in brackets describe the planes responsible for the various lines.

Chemical Analysis by X-rays.—The powder method may be made[1] an adjunct to quantitative analysis, which is of considerable usefulness. In a mixture of substances, each one gives its characteristic "pattern," and the relative intensities of the individual patterns are roughly proportional to the quantities present. A single example will be shown to illustrate this method of analysis. In Fig. 28 are shown photographs[2] of the



A. Pure $NaHF_2$. *B*. Sample for analysis. *C*. Pure NaF.

FIG. 28.—X-ray patterns of sodium fluoride and sodium hydrogen fluoride.

diffraction patterns of pure sodium fluoride, of a "sample," and of pure sodium hydrogen fluoride. All of the lines in the sample which do not correspond to one of these pure substances correspond to the other, which shows that only these two salts are present in considerable quantity. By prolonging the exposure, faint lines from traces of impurity can be brought out and identified from their resemblance to photographs of pure substances. A few cubic millimeters of substance is sufficient

[1] HULL, *J. Am. Chem. Soc.*, **41**, 1168 (1919).

[2] Courtesy of Dr. A. W. Hull of the General Electric Company.

for a complete analysis, and the material is not altered in any way while its composition is being determined.[1]

Structure of Surfaces.—From the arrangement of atoms in alkali halide crystals, it was seen that the identity of the molecules in them is lost; that the chemical attraction of an atom was equally distributed among the surrounding atoms, to no one of which it was specifically "combined;" it was equidistant from these atoms and equally "belonging" to each one. Of course, as the atoms evaporate from the crystal, they must do so in the requisite pairs or groups to form gaseous molecules. In other words, while molecules of salts do definitely exist in the gaseous state and probably in solutions, they appear to lose their existence as separate individuals in a crystal. The question occurs at once, What about atoms in the surface? Since in a crystal the chemical attractions act in all directions, the surface atoms must either have the attractions normally exerted in the outward direction bent in some interior direction and there satisfied; or else this attraction exists unsatisfied, and there is extending out into space (for the molecular distance of 10^{-8} cm. at least) a definite chemical attraction.[2] The latter view is probably correct, for when a crystal is suspended in a saturated solution of it, the crystal will attach to itself other layers and grow in size. This could hardly be the case if the attraction of the outside layers of atoms in a crystal were fully satisfied, and it therefore seems certain that there is at a solid surface some unsatisfied chemical attraction, capable of holding (more loosely than in strict chemical combination perhaps) other molecules on the surface.

[1] A detailed discussion of the applications of X-rays is given in *Trans. Faraday Soc.*, **15** (February, 1920). Here the experimental methods are reviewed and explained, and interesting examples of the results are given. See also W. L. Bragg, *Nature*, **105**, 646 (1920); and the texts by Wyckoff and by the Braggs.

[2] This attractive force exerts no appreciable effect beyond atomic distances. Langmuir (*J. Am. Chem. Soc.*, **38**, 2221 (1916)) has calculated that the attractive force between atoms becomes practically negligible when the distance between centers is twice as great as the distance at which the atoms are in equilibrium. He states also that the attractive force between atoms increases to a maximum when the distance between atoms is 0.6×10^{-8} cm. greater than the distance at which the attractive force is zero.

Adsorption.—This is a term now commonly used to denote the formation of layers of molecules attached to or attracted by a solid surface of some other material, in contrast to the *absorption* of a substance into the interior of another. Thus the layer of gas which adheres so strongly to glass surfaces is considered to be adsorbed; the coloring matter dissolved in sugar syrups is removed by adsorption on the surface of charcoal through which it is filtered. The structure of surfaces as outlined in the previous paragraph affords a ready explanation of adsorption, for the residual chemical affinity of the atoms in the surface layer holds the molecules of the adsorbed substance. All of the chemical attraction of the atoms in a surface is not free to adsorb other molecules, since part of it is exerted upon atoms within the solid, but the active portion of this force is purely chemical. Adsorption is thus a species of selective chemical combination, but in a somewhat looser way than that of the usual chemical reaction.

According to Langmuir,[1] when gas molecules impinge against any solid or liquid surface, they do not, in general, rebound elastically, but condense on the surface, being held by the fields of force of the surface atoms. These molecules may subsequently evaporate from the surface, and the length of time that elapses between the condensation of a molecule and its subsequent evaporation depends on the intensity of the surface forces. Adsorption is the direct result of this time lag. If the surface forces are relatively intense, evaporation will take place at only a negligible rate, so that the surface of the solid becomes completely covered with a layer of molecules. This layer will usually be not more than one molecule deep. If, on the other hand, the surface forces are weak, evaporation may occur so soon after condensation that only a small fraction of the surface becomes covered by a single layer of adsorbed molecules.

If this is the true explanation of adsorption, there would form a layer of gaseous molecules possibly one molecule deep; but the formation of a second layer would take place only through the attraction of the gas molecules in the first layer for more molecules of their same kind. This would, in effect, be the formation of a condensed (*i.e.*, liquid) layer of the gaseous molecules, which

[1] *J. Am. Chem. Soc.*, **40**, 1361 (1918).

we should not expect if the gas were far from its condensation pressure and temperature. Langmuir states that the forces (chemical forces) involved in adsorption of gaseous molecules on solid surfaces are very much larger than the forces acting between the molecules of liquids. If this is true, we should not expect the formation of a second layer of adsorbed gas, for this could be held only by the weaker forces acting between molecules of the gas. Further, adsorption takes place from very dilute gases, where the forces of attraction between molecules are known to be negligibly small. The formation of a layer one molecule deep is thus analogous to the spreading of oil films on water into a layer one molecule deep.

The forces holding an adsorbed *molecule* are of the same nature as those holding together the *atoms* of crystals; thus whether adsorption will take place or not, and to what extent, depends on the magnitude of these forces, *i.e.*, upon the residual valences of the atoms in the solid surface and in the adsorbed molecules. Such forces are typically chemical, and exhibit all the differences in intensity and quality characteristic of chemical forces.

No satisfactory equation has yet been developed for expressing the quantity of substance adsorbed on a given surface as a function of its pressure or concentration. The best-known attempt in this direction is the equation of Freundlich,[1]

$$q = a\, p^{1/n},$$

where q is the quantity of adsorbed substance, a is the proportionality constant, p is the pressure of the adsorbed substance, and n is a constant greater than unity, but different for different surfaces and gases. This equation is the best of the many proposed to cover adsorption, and it is satisfactory only as an interpolation formula. It fails to fit the facts even roughly when applied over a wide range of pressure. At low pressures the adsorption might well be expected to be proportional to the pressure (that is, to the number of molecules striking the surface); while as the pressure is increased the surface layer approaches saturation and there is no further increase of adsorption because there is no more uncovered surface at which the residual attraction of the surface atoms can act.

[1] *Kapillarchemie*, 1909.

In Table 39 are given the results of experiments by Langmuir on the adsorption of nitrogen on mica. These results were obtained by a simple and ingenious method. A quantity of mica whose area was 5750 sq. cm. was placed in one of two connecting bulbs of nearly equal volume, and both bulbs were very carefully and completely exhausted. A small quantity of nitrogen was admitted to the empty bulb and its pressure was determined. Then connection was established between this bulb and the one containing mica, and the pressure was measured again. The difference between the pressure to be expected from the relative volumes of the two bulbs and the pressure actually measured gave the quantity of nitrogen which had been adsorbed. Next the tube connecting the two bulbs was closed and the one containing no mica was carefully pumped out again. When the connecting tube was opened a second time, the difference between the expected and observed pressures was a measure of the amount of nitrogen adsorbed on the mica at the lower pressure.

TABLE 39.—ADSORPTION OF NITROGEN ON MICA AT 90° ABSOLUTE

Pressure (dynes per square centimeter)	Mols adsorbed $\times 10^6$	Calculated from Freundlich equation	Per cent deviation of Freundlich equation
34.0	1.37	1.54	+11
23.8	1.28	1.31	+ 3
17.3	1.17	1.14	− 3
13.0	1.06	1.01	− 5
9.5	0.995	0.883	−12
7.4	0.90	0.795	−11
6.1	0.79	0.726	− 7
5.0	0.707	0.68	− 4
4.0	0.628	0.62	− 1
3.4	0.556	0.58	+ 4
2.8	0.500	0.536	+ 7

The calculated values were obtained from the equation $q_p = 8.4\ p^{0.417}$. At the lowest pressure the slope of the plot (log p against log q) corresponded to $1/n = 0.68$; at higher pressures it decreases to $1/n = 0.20$.

In order to evaluate the constants of the Freundlich equation, log q was plotted against log p (solid line) and n was so chosen as to give a "straight line" through these points. As will be seen

from Fig. 29, the Freundlich equation (represented by a dotted line) is not a very satisfactory one for expressing adsorption as a function of the pressure.

Adsorption decreases as the temperature is raised. Therefore, when it is desired to remove an adsorbed film of gas from a solid surface, this is usually done by pumping out at a high temperature. Thus the evacuation of double-walled flasks for the storage of liquid air is usually carried out at a temperature just below the softening point of the glass. Since adsorption increases at lower temperatures, the evacuation of a flask may be made fairly complete by attaching it to a bulb filled with charcoal

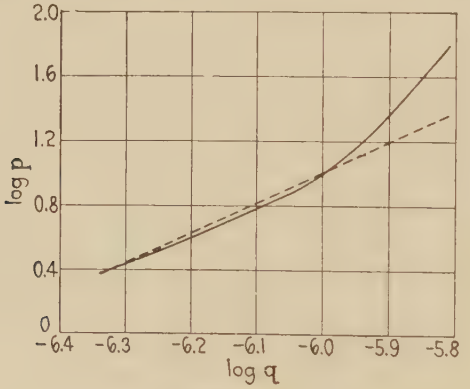


Fig. 29.

and immersing the charcoal bulb in liquid air while gently warming the flask to be evacuated.

Liquid Crystals.—Certain substances of complex organic nature melt to turbid liquids having quite different properties from those of ordinary liquids. As the temperature is further raised, a point is reached at which each liquid changes sharply to a clear liquid of ordinary properties. The substance thus shows, in addition to its usual "melting point," another transition temperature at which it assumes the properties of liquids. While in this intermediate state, the liquid exhibits double refraction, a property characteristic of crystalline substances. When a beam of light passes through a doubly refracting substance, there are two emerging beams, only one of which follows the ordinary

laws of refraction, and the rays are polarized. This occurrence is characteristic of substances which are not isotropic, that is, whose properties are not the same when measured in different directions. It follows that the intermediate "liquid" state is one in which the properties of the liquid are not the same in all directions. Lehmann[1] calls this intermediate condition the "liquid-crystalline" state; perhaps a better name would be doubly refracting liquids. Apparently weak forces such as those acting in crystals are at work arranging the molecules in a kind of space lattice similar to that of crystals, but less definite in character. The sharp disappearance of this double refraction at a definite temperature bears a resemblance to the melting point of crystals, except that in this case the substance is already fluid.

An early explanation of liquid crystals (Nernst, Bose) was that there were molecular swarms containing several atoms, but this idea has been found inadequate to explain the observations. Born[2] and Voigt[3] both consider that in liquid crystals there is an arrangement of the *molecules* in some particular way, perhaps parallel to one another with respect to some one axis, and that this is responsible for the behavior of liquids in this peculiar state. They do not say that there is definitely a space lattice similar to that in solid substances, but that if there is such a lattice it differs sharply from the one found in solids, in that it consists of molecules, not atoms. The identity of the molecules, even if lost in crystals, is assumed when they melt to form liquid crystals. At the second transition point, or clearing point, this molecular lattice is lost, and with it the double refraction characteristic of anisotropic substances.

Over 170 substances showing two transition points[4] have been prepared, and from a study of them it has been shown that there is no space lattice detectable by the usual X-ray methods applicable to solid substances. These liquid crystals have optical rotatory powers as high as 4000° for a film 1 mm. thick; a quartz

[1] A review of his very numerous papers on this subject is given in *Physik. Z.*, **19,** 73 (1918).

[2] *Sitzb. kgl. preuss. Akad. Wiss.*, **1916,** 614.

[3] *Physik. Z.*, **17,** 76, 152 (1917).

[4] *Engineering*, **106,** 349 (1918), a review of the subject.

plate of this thickness has a rotation of only about 25°. There is apparently no relation between the constitution of the compounds[1] and their capacity for producing liquid crystals. It may be that all organic substances are capable of forming liquid crystals, but the temperature ranges of their existence are so small that they have escaped detection. This is rendered unlikely by the fact that some of the substances exhibit their peculiar properties through a range of 35°. A few examples are mentioned in Table 40.

TABLE 40.—SUBSTANCES FORMING LIQUID CRYSTALS[2]

Substance	Transition temperatures, degrees		Range of existence of liquid crystals, degrees
Cholesterin benzoate	145	179	24
p-Azoxyanisole	118	136	18
p-Azoxyphenetole	134	169	35
Pyridine nitrate	88	105	17
Quinoline nitrate	102	119	17
p-Methylaminobenzaldehyde phenyl hydrazone	170	190	20
p-Ethylaminobenzaldehyde phenyl hydrazone	160	181	21

Questions

1. The melting point of monoclinic sulfur is 110° and it increases 0.05° per atmosphere. The density of monoclinic sulfur is 1.960 and its heat of fusion is 320 cal. per atomic weight. Calculate the density of liquid sulfur.

2. The vapor pressure of ice is 4.58 mm. at 0° and 3.30 mm. at −4°. Calculate the heat of sublimation of a gram of ice from the approximate form of the Clausius-Clapeyron equation.

3. Calculate the specific heat of ice from Kopps' law. Calculate the specific heat of iron oxide, and the percentage error. The measured specific heats are 0.54 and 0.16 respectively.

4. The sublimation pressure of bromine is 15.7 mm. at −21°, and 25 mm. at −15.5°. Calculate the latent heat of sublimation of bromine. Calculate from this value the sublimation pressure at −11°.

Ans. 68.2 cal. per gram; 35 mm.

[1] CHAUDHARI, *Chem. News*, **117**, 269 (1918).

[2] ROTARSKI, *Ber.*, **41**, 1994 (1908).

5. (*a*) Calculate the weight of nitrogen gas necessary to cover the surface of a cube of 1-liter capacity with a layer one molecule deep, making a reasonable assumption as to the diameter of an atom, and assuming both atoms of the molecule in contact with the adsorbing surface. (*b*) How large an error would the loss of these molecules produce in the calculated pressure at 20° and 1 atmosphere?

6. A cube which contains four molecules of a substance like sodium chloride is usually drawn as shown in Fig. 30. Calculate what part of each of the atoms shown belongs to this cube and show that it really contains 4NaCl.

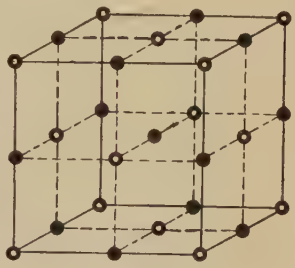


FIG. 30.

7. MgO has been shown to have the simple cubic arrangement and the edge of a cube containing 4MgO is 4.20 Å. Calculate its density. (Å signifies an Angstrom unit, 10^{-8} cm.)

8. Given the density of KI as 3.11, calculate the edge of a cube containing 4KI, assuming a simple cubic arrangement. The measured edge is 7.1 Å.

9. Copper crystallizes in the face-centered cubic arrangement; and the edge of the unit cube is 3.6 Å. Show that the density calculated upon the assumption of this arrangement is in agreement with the measured density, which is 8.93.

10. Cesium chloride forms a body-centered cube arrangement and the cube containing 1CsCl has an edge of 4.12 Å. Show that this arrangement is in conformity with its measured density and not in conformity with a simple cubic arrangement, in which most of the alkali halides crystallize. The density of CsCl is 3.97.

11. The film in Fig. 27 was bent on an arc of 8-in. radius from the specimen and the distance from the *transmitted* X-ray beam to the first-order 100 line for iron was 4.1 in. The X-ray beam was the K_α line for molybdenum and its wave length was 0.712×10^{-8} cm. Bearing in mind that the angle through which the X-rays have been deflected is 2θ, calculate the 100 plane spacing for iron.

12. The distance from the projected beam to the first-order 100 line for copper, under the conditions given in the previous problem, was 3.2 in. for X-rays of the same wave length. Calculate the 100 spacing for the planes of atoms in copper.

CHAPTER V

SOLUTIONS

A solution is a homogeneous phase in which two or more molecular species are present. We shall consider in this chapter only liquid solutions, that is, mixtures of two liquids or a liquid in which a gas or a solid has been dissolved, or dispersed into single molecules. So-called "colloidal solutions" contain molecular groups or aggregates which are very much larger than single molecules; they are, in fact, exceedingly fine suspensions of solids or liquids, and are considered later in a separate chapter. "Solid solutions" will be considered briefly under heterogeneous equilibrium; solutions of ionized substances are considered in the next chapter.

There are no fixed rules by which to predict whether a substance will dissolve in a given liquid or not, or to what extent. The probability that a solution can be formed increases with the resemblance of the solvent to the dissolved substance; hence most closely related liquids mix with one another in all proportions. Chemically unlike substances, such as water and silver nitrate or sodium chloride, also form solutions over a wide range of compositions; yet silver chloride scarcely dissolves in water at all. Carbon bisulfide is soluble in all proportions in alcohol, but very slightly soluble in water; though water and alcohol are soluble in one another in all proportions.

In dilute solutions one of the components of the mixture is present in large excess and is called the *solvent*, the dissolved substance being called the *solute*. It is convenient to express the composition of these solutions in terms of the number of mols or formula weights of solute present per liter of solution (volume concentration) or per thousand grams of solvent (formal concentration). The compositions of concentrated solutions are also expressed by mol fractions, as was done in mixtures of gases. The mol fraction of a substance in solution is the number of molecular weights of it present, divided by the number of

molecular weights of all substances present. An example will make this clearer. A solution containing 10 per cent by weight of alcohol ($C_2H_5OH = 46.00$) has a density of 0.9839. A liter of this solution weighs 983.9 grams and contains 98.39 grams or $98.39/46.00 = 2.14$ mols of alcohol. It contains also 885.5 grams or $885.5/18 = 49.4$ molecular weights of water; the mol fraction of alcohol is $\frac{2.14}{2.14 + 49.4} = 0.0416$. Similarly, the mol fraction of the water is 0.9584, since the mol fractions of all the substance present must add to unity. The concentration of this solution is 2.14 mols per liter of solution, or 2.42 mols per thousand grams of solvent, *i.e.*, 2.42 formal.

Ideal Solutions.—Certain substances form solutions whose properties may be expressed, in terms of the mol fractions of the components and the properties of the pure substances, by means of simple laws. These solutions are called "ideal solutions," and the laws expressing their properties are called the laws of ideal solutions. The volume of an ideal solution is equal to the sum of the volumes of the substances forming it; there is no heat evolved upon mixing the constituents; and the constituents of an ideal solution are able to dissolve in one another in all proportions. These statements may be regarded as a definition of an ideal solution. Most of the solutions encountered in chemistry are not strictly ideal solutions, and they are not, therefore, described accurately by the simple laws of ideal solutions; but for practical purposes many such solutions can be treated as ideal solutions, and their properties calculated in terms of those of the constituents. Just what is meant by "practical purposes" will depend upon the accuracy desired in the calculation. In treating the laws of ideal solutions we shall endeavor to form an opinion as to the deviations to be expected from the various types of solution, and of the limitations of the laws stated. Failure to appreciate that these laws have limited applicability will often lead to considerable errors; thus the vapor pressure of a solution of a mol of alcohol in a mol of water as calculated from the laws of ideal solutions is in error by 30 per cent.

Vapor Pressure of Solutions. Raoult's Law.—The vapor pressure of a solution is commonly understood to mean the

partial pressure of *solvent vapor* above the solution, but in case more than one constituent of the solution is volatile, each one has a partial pressure in the vapor over the solution. Addition of a solute to a solvent lowers the total vapor pressure of the solution in case the solute is not volatile. This lowering is proportional to the mol fraction of the added solute in an ideal solution, or the vapor pressure itself is proportional to the mol fraction of the solvent. Expressed in the form of equations, these two statements of Raoult's law (which are two ways of saying exactly the same thing) are as follows:

$$\frac{p_0 - p}{p_0} = x$$

and

$$p = p_0 x_0 = p_0(1 - x), \qquad (1)$$

where p_0 is the vapor pressure of pure solvent, and x_0 is its mol fraction in the solution; p is the vapor pressure of solvent from the solution, and x is the mol fraction of the solute. The *fractional* lowering of the vapor pressure is the same at all temperatures for a given solution, and is a measure of the mol fraction of the dissolved substance. In applying Raoult's law the vapor pressure of solvent and solution must always be determined at the same temperature.

Raoult's law offers a means of determining the molecular weights of dissolved substances from vapor-pressure lowering of solutions of known composition. In Tables 41 and 42 are

TABLE 41.—LOWERING OF VAPOR PRESSURE
(Naphthalene (formula weight 128) dissolved in benzene at 75°.)

Grams solute	Grams solvent	Mols solvent	Vapor pressure in millimeters	Molecular weight calculated
0.0000	26.53	0.340	639.85	
0.7913	26.53	0.340	628.7	131.3
1.3141	26.53	0.340	621.6	131.7
1.8411	26.53	0.340	614.5	131.3
2.3446	26.53	0.340	607.4	129.2
3.3453	26.53	0.340	594.3	128.5

ROSANOFF and DUNPHY, *J. Am. Chem. Soc.*, **36,** 1416 (1914).

given the vapor pressures of some solutions, together with the molecular weight of the solute calculated from Raoult's law. Table 43 shows the vapor-pressure lowering per mol of

TABLE 42.—BENZIL (FORMULA WT. 210) DISSOLVED IN ETHYL ALCOHOL AT 15°

Grams solute	Grams solvent	Mols solvent	Vapor pressure in millimeters	Molecular weight calculated
1.300	46.00	1	31.982	210
0.711	46.00	1	32.061	191
0.367	46.00	1	32.121	200
0.196	46.00	1	32.150	214
0.000	46.00	1	32.180	

TOWER and GERMANN, *J. Am. Chem. Soc.*, **36,** 2449 (1914).

TABLE 43.—SOLUTIONS OF MANNITE IN WATER AT 20°, p_0 = 17.51 MM.

Molal concentration per 1,000 grams water	Vapor pressure lowering		Per cent deviation of Raoult's law	Lowering per mol of solute (observed)
	Observed	Calculated from Raoult's law		
0.0984	0.0307	0.0311	1.3	0.3113
0.1977	0.0614	0.0622	1.3	0.3108
0.2962	0.0922	0.0931	1.0	0.3123
0.3945	0.1227	0.1239	1.0	0.3107
0.4938	0.1536	0.1547	0.7	0.3111
0.5944	0.1860	0.1858	0.1	0.3129
0.6934	0.2162	0.2164	0.1	0.3118
0.7927	0.2478	0.2469	0.3	0.3126
0.8922	0.2792	0.2775	0.7	0.3129
0.9908	0.3096	0.3076	0.6	0.3124

FRAZER, LOVELACE, and ROGERS, *J. Am. Chem. Soc.*, **42,** 1793 (1920).

solute in 1000 grams of water. The vapor-pressure lowering, expressed in terms of the weights of substances in solution, is

$$\frac{p_0 - p}{p_0} = x = \frac{m/M}{m/M + m_0/M_0}, \qquad (2)$$

where m is the weight of solute added to m_0 grams of solvent, M is the molecular weight of the dissolved substance, and M_0

is the molecular weight of the solvent. It will be seen that the deviation from Raoult's law is quite small.

Direct measurements of vapor pressure are more difficult, from an experimental point of view, than are certain other measurements (freezing-point depressions, boiling-point elevation) which are equivalent to vapor pressures. Such measurements will generally be found more useful in molecular weight determinations than vapor-pressure measurements.

Raoult's law applies strictly to dilute solutions, but does not accurately express the vapor pressure of most concentrated solutions in terms of the mol fraction of solute. Conversely, the mol fraction calculated from vapor-pressure measurements in strong solutions is unreliable. The following data will serve to illustrate the errors when concentrated solutions are involved.

TABLE 44.—VAPOR PRESSURE OF SUGAR SOLUTIONS AT 30°

Mols sugar per 1,000 grams water	Mol fraction of solute	Vapor pressure (millimeters)	$\frac{p_0 - p}{p_0} = x$	Per cent error in mol fraction calculated from Raoult's law
0.993	0.0175	31.22	0.0194	10
1.65	0.0288	30.76	0.0338	13
2.38	0.0410	30.21	0.0520	21
3.27	0.0555	29.43	0 0746	25
4.12	0.0690	28.72	0.0980	29
5.35	0.0877	27.55	0.1326	33
6.36	0.1025	26.70	0.1612	37

BERKLEY and HARTLEY, *Trans. Roy. Soc. London*, (A) **218**, 295 (1919).

Doubtless some of this error is due to combination of some sort between the sugar and water; or perhaps the molecular weight of liquid water is not 18. But at least these factors also exert an influence in other cases as well, so that the deviations here found may be considered typical of strong solutions.

Vapor Pressure of the Solute. Henry's Law.—The solubility of a gas at a given temperature is proportional to the pressure of the gas above the solution. Expressed as a vapor-pressure law, this states that the partial pressure of a volatile solute from

a solution is proportional to its mol fraction, or to its concentration. The equations are

$$p = kx \text{ or } p = k'C, \tag{3}$$

where p is the partial pressure of the gas above the solution, x is its mol fraction, and C its concentration in the solution. It will be seen that this law closely resembles Raoult's law, the difference being that the proportionality constant is not the vapor pressure of the pure gas in the equation for Henry's law. The value of the constants k and k' must be determined at each temperature by experiment; these constants are not the same for different solutes, or for the same solute at different temperatures or for various solvents. Henry's law is useful, therefore, only in calculating the solubility at some new pressure, or the vapor pressure of the solute at some new concentration, when the corresponding quantity is known for one solution at the temperature in question. Data illustrating this law are given in Table 45.

TABLE 45.—SOLUBILITY OF CARBON DIOXIDE IN WATER

At 100°			At 25°		
Pressure of CO_2 (atmospheres)	Molal concentration[1]	p/C	Pressure of CO_2 (atmospheres)	Molal concentration[2]	p/C
60	0.303	198	4.12	0.139	29.7
70	0.342	205	5.33	0.180	29.7
80	0.374	213	7.64	0.258	29.6
90	0.427	211	10.61	0.358	29.6
100	0.461	218	12.16	0.410	29.6
110	0.503	218	19.73	0.666	29.6
120	0.554	217	22.56	0.761	29.6
130	0.606	215	40.61	1.370	29.6
140	0.661	212			
150	0.695	216			
160	0.748	214			
170	0.770	221			

[1] SANDER, *Z. physik. Chem.*, **78**, 513 (1911).
[2] SMITH, *J. Am. Chem. Soc.*, **40**, 885 (1918).

Distribution between Phases.—It will be seen from Henry's law that the ratio of the quantity of solute per liter of solution

to the quantity of gas per liter above the solution is a constant, since the concentration in the gas phase is proportional to the pressure. This same conclusion has been found to apply to the ratio between the equilibrium concentration of solute in one liquid phase and that in another liquid phase in contact with it. For example, if a substance soluble in both water and benzene is dissolved in water, and this solution is shaken with a quantity of benzene, it will be found at equilibrium that the ratio of the molal concentration in the benzene layer to that in the water layer is a constant, regardless of the quantity of solute used, or of the relative quantities of benzene and water. Like the constant in Henry's law, the distribution constant must be determined by experiment for each solute and for each pair of mutually insoluble liquids, and the constant changes with the temperature. When two phases are in equilibrium with one another as regards some particular component and one of these is in equilibrium with a third phase, the other is also in equilibrium with this third phase. If the third phase is the solid solute itself, then when one liquid is saturated with the solid and in equilibrium with another liquid, this second liquid must also be a saturated solution of the solute. Thus the distribution constant for a given substance between two solvents is the ratio of the solubilities of that substance in the two phases, provided the distribution law holds for such concentrated solutions. Like Raoult's law and Henry's law, the distribution law is exact for very dilute solutions, and exhibits deviations in more concentrated ones. When the solutions (except those of ionized substances) are less than one formal, the deviations from these laws are usually less than 2 per cent.

Table 46 shows the distribution of succinic acid between water and ether, expressed as the mol fraction of the acid in each phase. The distribution law applies only to a *particular species of molecule*, and would not give a constant if succinic acid were in a different condition in the two phases; for example, if it were associated into double molecules in the ether layer, or if it were highly ionized in the water layer. When a set of distribution ratios calculated from experimental data shows a steady decrease or increase with the concentration, the most common explanation is the assumption of a different molecular condition of the solute

TABLE 46.—DISTRIBUTION OF SUCCINIC ACID BETWEEN WATER AND ETHER
(Concentrations are in mols of acid per 100 mols of solution.)

15°			20°			25°		
Water layer	Ether layer	k	Water layer	Ether layer	k	Water layer	Ether layer	k
0.372	0.305	1.223	0.2025	0.1535	1.322	0.364	0.248	1.471
0.440	0.358	1.229	0.431	0.319	1.351	0.720	0.485	1.485
0.575	0.468	1.228	0.495	0.366	1.353	1.088	0.727	1.493
0.880	0.714	1.233	0.629	0.465	1.355	1.513	0.731	1.489
0.963	0.778	1.237	0.936	0.686	1.364			
.....	.....	.....	1.211	0.889	1.363			

FORBES and COOLIDGE, *J. Am. Chem. Soc.*, **41**, 150 (1919).

in the two phases. Usually this is an association into double molecules in organic solvents containing no oxygen when the solute is an organic acid. The constant distribution ratio in Table 46 shows that succinic acid does not polymerize in ether solution, and does not ionize to any considerable extent in water solution. It will be noted that the distribution ratio for ammonia (Table 47) is not constant for concentrations much above molal. This is in harmony with the deviations of other laws in concentrated solutions. The distribution ratio of acetic acid between water and benzene changes rapidly with the concentration, as may be seen in Table 48. Acetic acid forms double molecules in the latter solvent, and single molecules in water, so that this is an improper application of the distribution law. The proper method of handling such cases will be taken up in the chapter on chemical equilibrium.

The distribution equation in terms of mol fractions and in terms of concentration is

$$\frac{x_1}{x_2} = k' \text{ or } \frac{C_1}{C_2} = k, \qquad (4)$$

where the subscripts refer to the two phases involved.

All three of the laws just considered, Raoult's law, Henry's law, and the distribution law, refer to the distribution of some *one molecular species* between two phases. Thus, Raoult's law states that the concentration of the *solvent* molecules above

a solution is proportional to their concentration in the solution; Henry's law says that the concentration of *solute* molecules above a solution is proportional to the concentration in it; and the distribution law refers to the ratio of the concentration of *solute* in two liquid phases in equilibrium with one another.

TABLE 47.—DISTRIBUTION OF AMMONIA BETWEEN WATER AND CHLOROFORM

At low concentration			At high concentration		
Concentration in water	Concentration in chloroform	C_w/C_c	Concentration in water	Concentration in chloroform	C_w/C_c
0.0443	0.00165	26.2	1.02	0.045	22.7
0.0220	0.00091	24.1	3.13	0.146	21.4
0.0110	0.00044	24.7	5.24	0.283	18.5
0.00572	0.00021	25.7	7.29	0.457	15.9
0.00275	0.00011	24.6	9.35	0.710	13.2
			12.25	1.227	10.0

Z. physik. Chem., **30**, 258 (1899). *J. Am. Chem. Soc.*, **33**, 940 (1911).

TABLE 48.—DISTRIBUTION OF ACETIC ACID BETWEEN BENZENE AND WATER AT 25°

(Acetic acid forms double molecules in benzene.)

C_B	C_w	C_B/C_w
0.0159	0.579	0.0274
0.0554	1.382	0.0401
0.2250	3.299	0.0776
0.9053	6.997	0.1290

Vapor Pressures of Ideal Solutions of Two Liquids.—When two liquids, A and B, form an ideal solution, the partial pressure of each in the vapor above a solution is proportional to its mol fraction in the solution, and these partial pressures may be calculated from Raoult's law. Thus

$$p = p_0 x \text{ and } p' = p_0' x'$$

where p_0 is the vapor pressure of pure liquid A and x is its mol fraction in the solution; and p_0' is the vapor pressure of pure

liquid B and x' is its mol fraction. The vapor pressures over the whole range of mol fractions from pure A to pure B for such an ideal solution are shown in Fig. 31, where the partial pressure of A is given by the line ga, that of B by bh, and the total vapor pressure (which is the sum of the two partial vapor pressures) by the line ba.

When the solution contains only A, $x = 1$, $x' = 0$, and the total pressure is p_0, the vapor pressure of pure A (ah in the figure). Similarly for pure B, $x = 0$, $x' = 1$ and the total pressure is p' (bg). When the substances are present mol for mol, $x = 0.5$, $x' = 0.5$, $p = 0.5p_0$, and $p' = 0.5p_0'$, corresponding to ce and cd respectively. The total pressure is the sum of these pressures, or cf. If ce and cd are the partial pressures, then the mol fractions in the vapor are $X_A = ce/cf$ and $X_B = cd/cf$; and these will be the mol fractions of the two substances in the *first portion* of distillate condensed from the solution at this temperature, since distillate is condensed vapor. As ce and cd are not equal, the mol fraction of constituent A in the vapor will not be the same as in the solution from which it came. In general, the greater the difference between the vapor pressures of the two components, the greater the difference in composition between a liquid and a vapor in equilibrium with it.

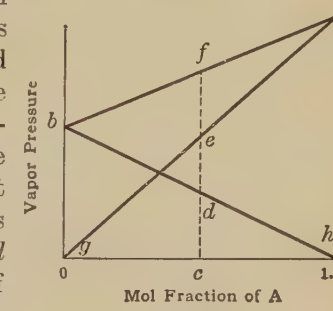


FIG. 31.

Ideal solutions of this kind are formed only when the two components are chemically very similar. For most pairs of liquids which mix in all proportions the deviations from ideal solutions are considerable when both constituents are present in large proportion, for example, when the mol fractions are between 0.1 and 0.9 for both. This may be due to the formation of complexes between solvent and dissolved substances, or to the dissociation of double molecules of solvent, either of which would render the mol fractions calculated from the composition by weight in error. The vapor pressures of mixtures of benzene and toluene are given in Table 49 and Fig. 32, together with the total vapor

pressure calculated from the sum of the partial pressures demanded by Raoult's law.

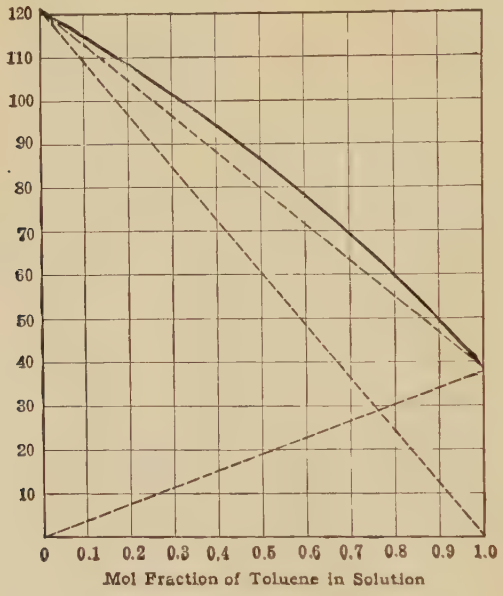


FIG. 32.

TABLE 49.—VAPOR PRESSURES OF MIXTURES OF BENZENE AND TOLUENE AT 30°

Mol fraction of toluene in solution	Exptl. total pressure	Calculated partial pressures		Calculated total pressure	Per cent error
		Benzene	Toluene		
0.00	121.8	121.8	....	121.8	
0.10	115.1	109.5	3.8	113.3	2
0.20	108.3	97.4	7.6	105.0	3
0.30	101.4	85.3	11.3	96.6	5
0.40	94.0	73.1	15.1	88.2	6
0.50	86.0	60.9	18.9	79.8	7
0.60	77.8	48.7	22.6	71.3	8
0.70	69.2	36.5	26.4	62.9	9
0.80	60.0	24.4	30.1	54.5	9
0.90	50.1	12.2	33.9	46.1	8
1.00	37.7	....	37.7	37.7	

SCHULZE, *Ann. Physik*, **59**, 82 (1919).

As the two components are chemically very similar, there is every reason to expect approximate agreement with the laws of ideal solutions, and this may be taken as a good example of the agreement generally obtained.

Benzene and carbon disulfide form a solution which deviates somewhat more from an ideal one. The total vapor pressure at 30°, and the partial pressures of each substance from solution are shown in Table 50. The total pressure was measured with a manometer, and each partial pressure was computed from the mol fraction of it in a small portion of distillate collected.

TABLE 50.—VAPOR PRESSURES OF SOLUTIONS OF BENZENE AND CARBON DISULFIDE[1] AT 30°

Mol fraction of benzene in solution, 30°	Total vapor pressure in millimeters	Partial pressure of benzene millimeters	Partial pressure of CS_2 millimeters	Pressure of CS_2 calculated from Raoult's law	Per cent deviation
0.00	434.6	.....	434.6		
0.0800	413.1	14.7	398.4	399	0
0.2286	378.9	35.8	343.1	335	2.5
0.3723	340.8	53.3	287.5	272.5	5
0.6516	259.1	81.6	177.5	151	15
0.8845	169.5	107.3	62.2	50	19
1.000	119.3	119.3			

The large errors in the pressure of carbon disulfide calculated by means of Raoult's law when it is present in small proportion illustrate an important fact. Raoult's law is a law for the vapor pressure of a *solvent*, and carbon disulfide is scarcely the solvent when its mol fraction is only $1 - 0.885 = 0.115$, as it is in the next to last line of the table. If the vapor pressure of *benzene* from this solution is calculated from Raoult's law, it is $119.3 \times 0.8845 = 105.5$, which is in error by about 2 per cent.

Mixtures of acetone and carbon bisulfide[2] may be taken as an extreme example of the deviations of Raoult's law. Here the total vapor pressure of an equimolal solution is far higher than that of either pure component, and the partial pressure of carbon bisulfide from this solution is 20 per cent higher than that calculated from Raoult's law. For these solutions no simple

[1] SAMESHIMA, *J. Am. Chem. Soc.*, **40**, 1503 (1918).

[2] ZAWIDSKI, *Z. physik. Chem.*, **35**, 172 (1900).

laws are known. The composition of vapor in equilibrium with each solution is shown by the dotted line below the total vapor-pressure curve. For example, the solution whose composition is a (Fig. 33), is in equilibrium with vapor of composition b.

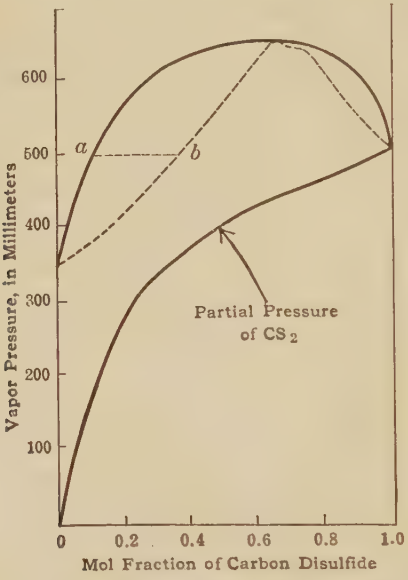


FIG. 33.—Acetone—CS_2 mixtures at 35°.

Constant Temperature Distillation.—By reference to the fourth line of Table 50 it will be seen that the partial pressures of benzene and of carbon disulfide are respectively 53.3 and 287.5 mm. over a solution in which the mol fraction of benzene is 0.3723. The partial pressures in the vapor phase are proportional to their mol fractions in the vapor (Dalton's law), each pressure being the product of the mol fraction and the total pressure. Hence the mol fractions in the vapor phase are $53.3/(53.3 + 287.5) = 0.156$ for benzene and $1 - 0.156$ or 0.844 for carbon disulfide. If this vapor is cooled so that it condenses completely, the mol fractions in the condensed liquid will be the same as in the vapor from which it is formed, 0.156 and 0.844. This is exactly what happens in distillation; a vapor is expelled from a solution, and in this vapor the constituents are present in the ratio of their vapor pressures over the solution; this vapor con-

denses to a liquid having the same composition as the vapor, but a different composition from the solution out of which it was distilled.

TABLE 51.—BENZENE AND CARBON DISULFIDE AT 30°

Mol fraction benzene in solution	Partial pressure benzene, millimeters	Partial pressure CS_2, millimeters	Mol fraction benzene in vapor
0.0800	14.7	398.4	0.0355
0.2286	35.8	343.1	0.0945
0.3723	53.3	287.5	0.1564
0.6516	81.6	177.5	0.3151
0.8845	107.3	62.2	0.6333

Of course, if the *whole* solution were distilled, the total distillate would have the same composition as the original solution. But the *first portion* of distillate is richer in carbon disulfide than the original solution, and the liquid remaining behind will be poorer in carbon disulfide. In Table 51 are given the mol

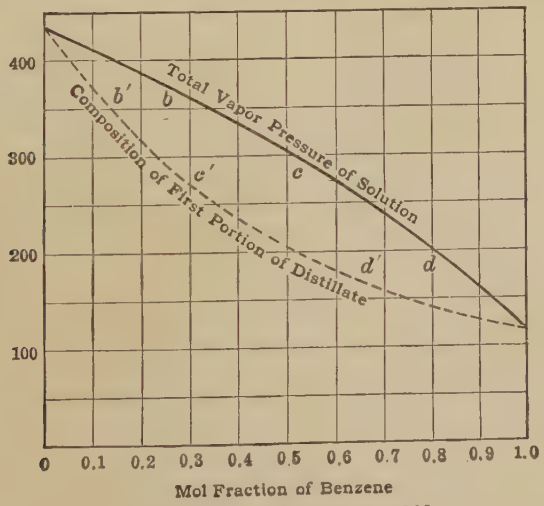


FIG. 34.—Benzene and CS_2 at 30°.

fractions of benzene in the vapor over each of the solutions of Table 50; it will be seen that each distillate contains a smaller proportion of benzene than the liquid from which it was expelled. The dotted line of Fig. 34 is so drawn that each point on it shows

the composition of vapor in equilibrium with the solution whose composition is shown by the solid line horizontally across from it. Thus a solution in which the mol fraction of benzene is 0.6 has a vapor pressure shown by c, and gives a vapor whose composition is shown by c', about 30 mol per cent benzene; and this vapor condenses to a liquid of the same composition.

We have so far assumed a constant temperature of 30° for the fractional distillation, and let the total pressure be whatever it might. In practice the pressure is kept constant, usually at 1 atmosphere, and the solution is brought to this total pressure by raising the temperature until the solution boils. This case will be considered after the boiling of solutions containing only one volatile component has been presented.

Boiling Point of Solutions.—The boiling point of any liquid or solution is the temperature at which the total vapor pressure is equal to that of the atmosphere, 760 mm. of mercury. Solutions, like pure liquids, increase their vapor pressures as the temperature is raised, but at any given temperature (for example, at the boiling point of the solvent) the pressure of solvent vapor from a solution is less than that from the pure solvent. The vapor-pressure lowering is proportional to the mol fraction of the dissolved substance, as indicated by Raoult's law. It will, therefore, be necessary to heat a solution to a temperature above the boiling point of the solvent before its vapor pressure becomes 1 atmosphere, in case the solute has no vapor pressure. A diagram of these conditions near the boiling point of a solution is given in Fig. 35; the solid line represents the vapor pressure of pure solvent and the dotted line the vapor pressure of a solution in which the mol fraction of the non-volatile solute is x.

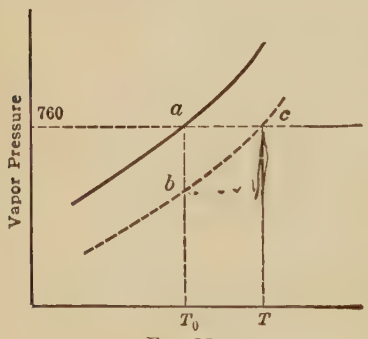


FIG. 35.

The vapor pressure of the solution at T_0, the boiling point of the solvent, is less than 760 mm. by the distance ab; to bring the pressure up to 760, so that the solution can boil, the temperature must be raised (while the vapor pressure increases along the dot-

ted line) until the point c is reached, at the temperature T. The relation between the lowering of the vapor pressure and the boiling-point raising is $ab/ac = (p_0 - p)/(T - T_0)$. But ab/ac is the slope of the dotted line, that is, it is the rate of change of the vapor pressure of the solution with the temperature. It will be seen that the dotted and solid lines are nearly parallel, however, at least for the short distances involved in a small change of boiling point, and hence we may write dp_0/dT for ab/ac, in place of dp/dT; that is, employ the change of vapor pressure of the pure solvent with the temperature in place of the change in vapor pressure of the solution with the temperature. Then we may write

$$\frac{p_0 - p}{T - T_0} = \frac{dp_0}{dT} = \frac{p_0 x}{T - T_0} \quad (5)$$

by substituting for $p_0 - p$ its value $p_0 x$ from Raoult's law on page 132. On solving this equation for the elevation of the boiling point, ΔT_b, we have

$$T - T_0 = \frac{p_0 x}{dp_0/dT} \text{ or } \Delta T_b = kx, \quad (6)$$

since the terms p_0 and dp_0/dT are characteristic of the solvent. The value of k will not be the same for all solvents, but must be determined in one of the ways explained below. The validity of this equation is illustrated by solutions of diphenyl in benzene.[2]

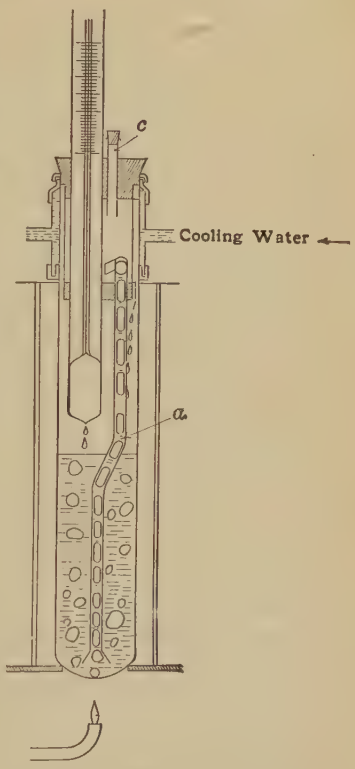


FIG. 36.—Boiling-point apparatus.[1]

[1] The narrow tube a serves to pump an intimate mixture of solution and vapor over the thermometer. Weighed pellets of solute are introduced through c, or the solution may be analyzed after a determination. The condenser is so arranged that cold solvent returning to the solution from it does not touch the thermometer, but runs down the pump tube.

Two pieces of boiling-point apparatus, like that shown in Fig. 36,[3]

[2] WASHBURN and READ, *J. Am. Chem. Soc.*, **41**, 729 (1919).

[3] COTTRELL, *J. Am. Chem. Soc.*, **41**, 721 (1919).

were used, one of which contained pure benzene and the other the solution. The boiling points of the solvent and solution were determined at the same moment, thus avoiding any error due to a change of atmospheric pressure during the progress of an experiment. The results for several solutions are shown in Table 52.

TABLE 52.—SOLUTIONS OF DIPHENYL IN BENZENE

Boiling point elevation	Mol fraction solute exptl.	Mol fraction solute calculated	$\frac{\Delta T}{x} = k$	Per cent error
1.333	0.0380	0.0387	35.7	1.8
1.709	0.0490	0.0494	35.0	0.7
2.152	0.0613	0.0618	35.1	0.8
2.521	0.0718	0.0717	35.0	0.1
3.142	0.0890	0.0885	35.3	0.5

In laboratory practice, the composition of a solution is commonly expressed in terms of the mols of solute per 1000 grams of solvent, and the elevation of the boiling point produced by a mol of solute in 1000 grams of solvent is called the *molal elevation of the boiling point, B*. For example 1000 grams of water is 1000/18 or 55.5 mols of water, and when a mol of solute is dissolved in 1000 grams of water its mol fraction is $x = 1/(1 + 55.5) = 0.0177$. The vapor pressure of water at its boiling point changes at the rate of 0.0353 atmosphere per degree, whence from equation (6), $p_0 = 1$, $dp_0/dT = 0.0353$, and

$$\Delta T_b = \frac{0.0177}{0.0353} = 0.502°$$

for a solution of a mol of solute in 1000 grams of water. If a correction is made for the deviation of water vapor from the laws of an ideal gas, the molal elevation becomes 0.518°. Then the boiling point elevation of any aqueous solution of a non-volatile substance is

$$\Delta T_b = 0.518C = BC, \qquad (7)$$

where C is the concentration of the solute in mols per 1000 grams of water. The values of this constant B for several liquids are given in Table 53. It will be seen that this equation furnishes a convenient means of determining the molecular weights of

dissolved substances, since the mols per 1000 grams of solvent is given by equation (7) from the boiling-point elevation, and the grams of solute per 1000 grams of solvent is known from analysis.

In equation (6) above the temperature coefficient of vapor pressure of the solvent, dp_0/dT, was used to determine the elevation of the boiling point, and the values in Table 53 were calcu-

TABLE 53.—MOLAL BOILING-POINT CONSTANTS[1]

Substance	Boiling point at 760 mm.	dp/dT atmospheres per degree	Molal boiling point raising, B	Correction for each 100 mm. change in total pressure
Acetic acid	118.51	0.0308	3.28	0.008
Benzene	80.15	0.0309	2.58	0.024
Carbon disulfide	46.00	0.0325	2.40	0.020
Chloroform	60.19	0.0329	3.64	0.010
Carbon tetrachloride	76.50	0.0314	5.05	0.036
Ethyl alcohol	78.26	0.0379	1.24	0.010
Ethyl ether	34.42	0.0358	2.21	0.007
Ethyl acetate	77.13	0.0317	2.90	0.012
Hexane	68.59	0.0313	2.89	0.007
Methyl alcohol	64.67	0.0399	0.84	0.009
Methyl acetate	57.11	0.0345	2.20	0.009
Methyl propionate	79.59	0.0330	2.77	0.016
Octane—*n*	125.80	0.0284	4.37	0.005
Pentane—*n*	35.98	0.0354	2.13	0.012
Propyl alcohol	97.14	0.0365	1.71	0.012
Propyl acetate	101.68	0.0299	3.61	0.010
Stannic chloride	114.20	0.0263	10.32	0.100
Water	100.00	0.0358	0.518	0.007

The corrections in the last column are to be added to B for every 100-mm. increase in the barometric pressure over 760 mm., and to be subtracted for every 100 mm. below 760 mm. For example, the molal elevation for stannic chloride at a pressure of 700 mm. would be 10.26°.

lated from the slope of this curve. It will be recalled that the approximate Clausius-Clapeyron equation expresses this change of vapor pressure in terms of the molal latent heat of evaporation. By substituting $dp_0/dT = p_0\Delta H_m/RT_0^2$ in equation (5) we have

$$\frac{dp_0}{dT} = \frac{p_0\Delta H_m}{RT_0^2} = \frac{p_0 x}{T - T_0}$$

[1] ROSANOFF and DUNPHY, *J. Am. Chem. Soc.*, **36**, 1415 (1914).

and on solving for ΔT we have

$$\Delta T = \frac{RT_0^2}{\Delta H_m} x = kx, \text{ or } \Delta T = BC. \tag{8}$$

For comparison, let us calculate a value of B for water from this equation, where B is the boiling-point elevation for a molal solution. The heat of evaporation of water is 538 cal. per gram, or 9700 cal. per mol, whence for 1 mol of solute per 1000 grams of water

$$\Delta T = \frac{1.99 \times (373)^2}{9700} \times \frac{1}{1 + 55.5} = 0.508°.$$

The agreement is about what may be expected in calculations involving the approximate equation $dp/dT = p_0 \Delta H_m / RT_0^2$. When data for the molal heat of evaporation are not at hand, approximate values suitable for use in equation (8) may be calculated from Trouton's rule, or its modifications. Conversely, the elevation of the boiling point may serve to determine the heat of evaporation, provided deviations of 2 or 3 per cent are not objectionable.

Fractional Distillation.—In the paragraphs just given, it has been assumed that the dissolved substance was not volatile. In some of the liquid mixtures mentioned earlier, each component has an appreciable vapor pressure, and the total vapor pressure may be greater or less than that of one of the components. For example, addition of acetone to toluene lowers the boiling point, since the partial pressure of acetone from such a solution is greater than the decrease in partial pressure of toluene produced by adding a solute. If the total pressure is higher than the vapor pressure of pure toluene at the same temperature, the solution will exert a pressure of 1 atmosphere at a temperature lower than toluene boils, and will, therefore, have a lower boiling point. Distillation is ordinarily carried out at a constant pressure of 1 atmosphere, and fractions of distillate passing over at different temperatures may be collected. The total vapor pressure remains constant, and the mol fraction of each substance in the distillate passing off from any liquid mixture is equal to its mol fraction in the vapor at equilibrium with this solution, these mol fractions in the vapor being a measure of the partial vapor pressures from solution. The boiling points of mixtures of acetone

and toluene are shown in Table 54, together with the partial pressure of each substance in the vapor in equilibrium with these solutions. For example, a mixture containing 68.6 mol per cent of acetone boils at 64°, that is, exerts a total vapor pressure of 760 mm. of mercury at this temperature, of which total pressure 696 mm. is due to acetone and 64 mm. to toluene. Since partial pressures are proportional to mol fractions in a gaseous mixture, the mol fraction of acetone in the vapor above this solution is 696/760, or 0.916; that of toluene is 64/760, or 0.084; and these are the mol fractions in the first portion of distillate passing over, since the distillate is formed by condensation of this vapor.

TABLE 54.—VAPOR PRESSURES OF TOLUENE-ACETONE MIXTURES

Mol fraction acetone in solution	Boiling point of solution	Partial pressure of acetone	Partial pressure of toluene	Mol fraction of acetone in vapor
0.00	109.4	0	760	
0.108	93.5	341	419	0.449
0.187	85.0	484	276	0.636
0.383	72.8	616	144	0.811
0.572	67.0	671	89	0.883
0.686	64.0	696	64	0.916
0.790	61.2	715	45	0.941
0 871	59.5	732	28	0.964
0.938	58.0	746	14	0.981
1.000	56.5	760	...	1.000

ROSANOFF, BACON, and WHITE, *J. Am. Chem. Soc.*, **36**, 1803 (1914).

In Fig. 37 the boiling points of the mixtures are plotted against mol fractions in the liquid, shown by a solid line; and the composition of the vapor in equilibrium with each solution is shown as a dotted line. Thus a solution of 25 mol per cent acetone boils at 80°, giving a first distillate which contains about 70 mol per cent of acetone. If the boiling is continued until 85° is reached, the last portion of distillate passing over has a composition of 64 mol per cent acetone, and the composition of the residual liquid is 19 mol per cent acetone. The composition of the total distillate is intermediate between 70 and 64 mol per cent. Reference to the solid line of Fig. 37 shows that this distillate (assuming it 67 mol per cent acetone) would boil at

about 64° and yield upon redistillation a first distillate containing nearly 90 mol per cent of acetone. By repeating these fractionations a mixture richer in acetone is obtained as a distillate each time, and by combining the residues and distilling out new portions it is possible to resolve such a mixture into its components after a number of repetitions of this process. This is true of mixtures when the boiling points of all solutions are between those of the components, provided these components do not have boiling points too close to each other.

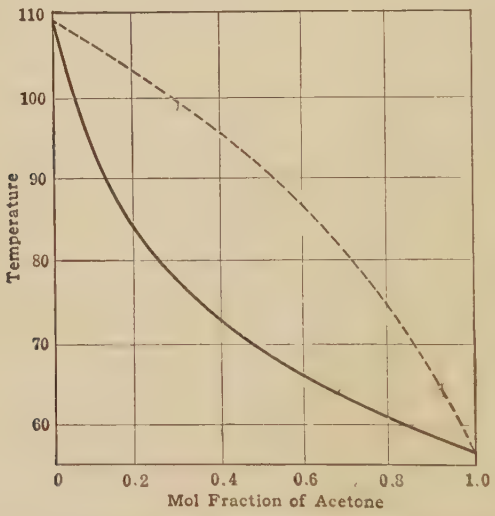


Fig. 37.—Boiling-point curve for mixtures of acetone and toluene.

Mixtures with a Minimum Boiling Point.—Certain pairs of liquids form mixtures which boil lower than either of the constituents; such mixtures cannot be separated by distillation into the two pure components, but only into one pure liquid and a mixture having the lowest boiling point. For example, acetone and carbon bisulfide form a solution with a higher vapor pressure than either component (page 142); this solution will, therefore, boil at a lower temperature than either pure component.

Similarly, methyl alcohol (boiling point 66°) and chloroform (boiling point 62°) form a mixture boiling at 54°, which mixture

contains about two mols of chloroform for one of alcohol. The boiling-point curve is shown by a solid line in Fig. 38 and the composition of distillate passing off at each boiling temperature is shown by the dotted line. A mixture of one mol of each substance boils at about 55°, yielding as a first distillate a mixture in which the mol fraction of chloroform is about 0.60. Complete fractionation of this mixture would yield pure methyl alcohol as a final residue, and the minimum boiling mixture as a final distillate. Any mixture containing over 66 mol per cent of chloroform may be fractionated into pure chloroform as a residue and the minimum boiling mixture as a final distillate.

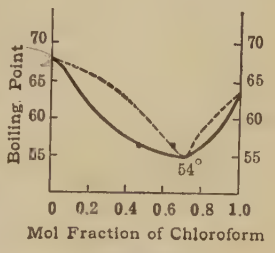


FIG. 38.

To each portion of the diagram of Fig. 38 may be applied the reasoning considered in connection with Fig. 37, where there was no minimum point. Ethyl alcohol and water are another pair of liquids forming a minimum boiling mixture, the 96 per cent alcohol of commerce. Certain other liquids form maximum boiling mixtures; they may be separated by fractionation into a distillate which is one pure component, and the maximum boiling mixture as a final residue; but not into the two pure components.

It frequently happens that maximum points or minimum points occur at percentage compositions which correspond to a simple molecular ratio of the two components. This is not very good evidence that a compound is formed, however. For example, constant boiling hydrochloric acid has a composition closely approximating $HCl.8H_2O$ when distilled under a pressure of 1 atmosphere; a weaker acid solution expels more water than hydrogen chloride and becomes stronger; a more concentrated acid loses hydrogen chloride faster than it loses water, and becomes weaker in acid until this constant boiling composition is reached. A constant boiling acid solution of somewhat different composition is obtained when the distillation is carried out under reduced pressure or increased pressure, so that the existence of a loose chemical compound in solution must be established by some other means than a maximum point in the boiling temperature curve. Minimum points are possibly an

indication of loose chemical combination between the constituents of a mixture, but in the lack of other and better evidence it is probably unsafe to assume that such compounds exist.

Distillation with Steam.—In all of the discussion of distillation given above, it has been assumed that there was only one liquid phase present. There is another type of distillation involving two phases, that is, two liquids which do not dissolve in one another. In this case each liquid exerts its own vapor pressure independently of the other liquid, and since the liquids are mutually insoluble, neither lowers the vapor pressure of the other by decreasing its mol fraction. When the total vapor pressure reaches that of the atmosphere, distillation takes place from both phases, and the mol fraction of each substance in the vapor passing over is proportional to its vapor pressure at the temperature of the distillation.

Consider, for example, a mixture of water and turpentine ($C_{10}H_{16}$) under a total external pressure of 1 atmosphere. When the temperature is 90° the vapor pressure of water is 526 mm. of mercury, and that of turpentine is 91 mm. At 100° the vapor pressures are 760 and 131 mm. The total pressures at each temperature are the sums of the two vapor pressures, since each liquid is substantially insoluble in the other; therefore the total pressure is 617 at 90° and 891 at 100°. Then at 90° the total pressure is below that necessary for boiling the mixture, and at 100° it is considerably above the necessary temperature. At 95° the vapor pressures for the two pure substances are 634 and 110, total 744. It is clear that the mixture will boil slightly above this temperature.

The mol fraction of each substance in the vapor is proportional to its partial pressure, and the mol fraction of each substance in the distillate is the same as that in the vapor. Since the partial pressure of turpentine at 95° is about 0.15 atmosphere, and that of water is 0.85 atmosphere, under a total pressure of 1 atmosphere these are the mol fractions of the two substances in the distillate. Then there will be 0.15 mol of turpentine for 0.85 mol of water, or 57 per cent of turpentine by weight. It should be noted that this process has effected the distillation of turpentine at about 95°, which is about 70° below its boiling point when distilled alone. Steam distillation is often resorted to in organic

preparations when a substance decomposes at temperatures near its normal boiling point.

A distillation with steam can also be carried out for liquids which are mutually soluble to a small extent, such as water and aniline; but the temperature at which such a distillation will take place cannot be computed from vapor-pressure data for the pure substances. In general, when the two liquids concerned are mutually soluble to a slight extent, the temperature of distillation is higher than if they were completely insoluble, but below the boiling point of either pure substance. Certain insoluble solid substances may be sublimed with steam also, since the current of steam serves to carry away saturated vapor as fast as it is formed, and the solid substance separates out when the vapor is cooled. When it is desired to distil or sublime substances of very small vapor pressures, superheated steam is often employed.

Freezing Point of Solutions.—The freezing point of a solution may be defined as the temperature at which the solution exists in equilibrium with the solid solvent; it is the temperature at which the solid solvent would begin to separate if the solution were cooled slowly. The addition of a solute will lower the vapor pressure of a solvent in accordance with Raoult's law, but will leave the vapor pressure of ice (in which the solute does not dissolve) unchanged. Thus the solution and ice will no longer be in equilibrium (have the same vapor pressure) at the freezing point of pure solvent. The sublimation pressure of ice decreases more rapidly as the temperature falls than does the vapor pressure of the solution, which changes at almost the same rate as the vapor pressure of pure solvent. Hence by lowering the temperature we may bring the solution and pure solid solvent to the same vapor pressure, that is, to equilibrium.

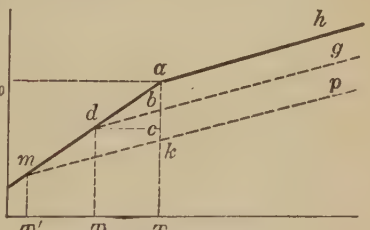


FIG. 39.

Let *ah* in Fig. 39 represent the vapor pressure of pure liquid solvent, *dbg* that of a solution in which the mol fraction of dissolved substance is x, and let *adm* represent the vapor pressure of

ice. At d the vapor-pressure lines for ice and the solution intersect; this is, therefore, the freezing point of the solution. It is desired to find the relation between ab, the vapor-pressure lowering (connected with the mol fraction through Raoult's law), and dc, the lowering of the freezing point produced by the dissolved substance.

In the figure ab is $ac - bc$, and the relation ab/dc is $(ac/dc) - (bc/dc)$. Now ac/dc is the slope of the line showing the change of the vapor pressure of ice with the temperature and bc/dc is the slope of the vapor-pressure curve for water. As in the previous derivation of the boiling-point equation, we may calculate the slope bc/dc from the approximate form of the Clausius-Clapeyron equation. This equation may also be applied to the change of the vapor pressure of a solid, using ΔH_s as the molal heat of *sublimation* of the solid, and the difference in volume between the saturated vapor and the solid forming it as the volume increase. Expressed as equations, these two slopes are

$$\frac{ac}{dc} = \frac{dp_i}{dT} = \frac{p_0 \Delta H_s}{RT_0^2} \text{ and } \frac{bc}{dc} = \frac{dp_0}{dT} = \frac{p_0 \Delta H_v}{RT_0^2},$$

where RT_0/p_0 is the volume of a mol of vapor. Upon subtracting one of these equations from the other, and noting that ab/dc is $(p_0 - p)/(T_0 - T)$, from the figure, we have

$$\frac{ac - bc}{dc} = \frac{ab}{dc} = \frac{[\Delta H_s - \Delta H_v]p_0}{RT_0^2} = \frac{p_0 - p}{T_0 - T}. \tag{9}$$

Further, put for $p_0 - p$ its equivalent $p_0 x$ from Raoult's law, and for the difference between the heats of sublimation and evaporation substitute its equal, the molal heat of fusion, ΔH_f, and the equation becomes

$$\Delta T = T_0 - T = \frac{RT_0^2}{\Delta H_f} x = F'x, \tag{10}$$

which is the desired equation. From it may be calculated the mol fraction x of a solute in a solution, provided its freezing point has been determined; or the freezing point may be calculated if the mol fraction of solute is known.

It will be seen from the figure that the triangles abd and akm are similar, and that mkp is the vapor pressure of a solution containing a larger mol fraction of dissolved substance in the solution. The vapor pressures of other solutions would be shown by lines

parallel to these lines *dbg* and *mkp*. Hence the lowerings of vapor pressure (which are proportional to the mol fraction of the solute) are proportional to the lowerings of the freezing points.

This freezing-point equation is valid only for dilute solutions; it should not be applied if the depression of the freezing point is more than 1 or 2°.[1]

The freezing point equation may also be expressed in terms of the mols of solute per 1000 grams of solvent, as was done for the boiling-point equation, since in equation (10) $RT_0^2/\Delta H_f$ is constant, and the mol fraction is nearly proportional to the concentration in dilute solutions. This equation is

$$\Delta T_f = FC \tag{12}$$

where the molal freezing-point lowering F, corresponding to a solution of 1 mol of solute in 1000 grams of solvent, is $RT_0^2/\Delta H_f$ divided by one plus the number of mols of solvent in 1000 grams. Equation (12) states that the freezing-point lowering in any sol-

TABLE 55.—MOLAL FREEZING-POINT CONSTANTS

Substance	Melting point	Molal lowering	Substance	Melting point	Molal lowering
Acetic acid	17	3.9	Bromine	−7.3	9.7
Formic acid	8	2.8	Stannic bromide	26.4	24.3
Water	0	1.855	Ethylene bromide	10	12.5
Benzol	5.5	5.12	Benzil	94	10.5
Naphthalene	80	6.8	Tribromphenol	95	20.4
Benzophenone	48	9.8	*p*-Xylol	16	4.3
Nitrobenzol	5.3	7.0	Aniline	− 6	5.9
Urethane	49	5.14	Acetamide	82	3.6
Carbon tetrachloride	−24	29.8	Chloroform	−61	4.68

Landolt and Börnstein's Tables, p. 793.

[1] A more exact equation connecting the freezing point with the mol fraction is

$$\frac{d\ ln\ (1-x)}{dT} = \frac{\Delta H_f}{RT_0^2}. \tag{11}$$

When the depression of the freezing point is large, ΔH_f must first be expressed as a function of the temperature before the equation is integrated. For dilute solutions the integral of this equation reduces to equation (10).

vent is proportional to the solute concentration, and that this lowering for a single mol of solute in 1000 grams of solvent is $F°$. The numerical value of the proportionality constant F is different for different solvents. Values of it for the more common solvents are recorded in Table 55.

Molecular Weights.—Freezing-point depressions offer the most convenient means of determining molecular weights in solution. They have two distinct advantages over boiling-point elevations, in that the latter are considerably influenced by changing atmospheric pressure during the progress of a determination, while freezing-point depressions are not affected, and the molal depressions of the freezing point are usually larger than the corresponding elevations of the boiling point for the same solvent. Also, at the low temperatures of freezing solutions there is less danger of losing solute by evaporation. The boiling-point equation, it will be recalled, was derived for a solute which was not volatile, but nothing was said about the vapor pressure of the solute in deriving the freezing-point equation. The freezing point of an aqueous solution is the temperature at which the vapor pressure of ice is equal to the partial pressure of water vapor above the solution, and it is independent of whether the solute has a vapor pressure or not.

By means of thermocouples it has been possible to measure very accurately the freezing points of quite dilute solutions. Usually the solution is made up somewhat stronger than needed, and poured over a quantity of crushed ice. The mixture is stirred until equilibrium is established, the freezing temperature is accurately determined, and a sample of the solution is withdrawn through a chilled filter and analyzed. This procedure is more accurate than that of chilling a solution of known concentration until ice begins to separate, for a correction must then be applied to allow for the ice which has separated. When a large quantity of ice is used, equilibrium is more readily and more certainly established, but it is often more difficult to determine the concentration of solution after freezing than to make it up of known strength. In Table 56 the freezing points of dilute solutions of mannite are shown; in Table 57 some illustrations of molecular weight determinations upon solutes dissolved in naphthalene are given.

TABLE 56.—SOLUTIONS OF MANNITE IN WATER[1]

Molal concentration	Freezing point depression	Lowering per mol of solute
0.006869	0.01274	1.853
0.01006	0.01846	1.847
0.01041	0.01930	1.855
0.02039	0.03790	1.859
0.02249	0.04171	1.854
0.05061	0.09460	1.868
0.06062	0.11265	1.858
0.09574	0.1790	1.870
0.1197	0.2225	1.858

TABLE 57.—FREEZING POINTS OF NAPHTHALENE SOLUTIONS

Solute	Grams in 25 grams naphthalene	Lowering of freezing point	Molecular weight calculated from ΔT_f	Formula weight
Nitrobenzene	0.2540	0.57	122.9	123.1
	0.5080	1.13	123.9	
	0.7580	1.70	123.1	
Aniline	0.2407	0.72	92.1	93.1
	0.364	1.08	93.0	
	1.008	2.99	93.0	
Benzoic acid	0.361	0.83	120.0	122.1
	0.522	1.15	125.3	
	0.748	1.69	122.2	

KOZICKI and PILAT, *Z. angew. Chem.*, **29**, (I), 423 (1916).

Osmotic Pressure.—The molecules of a dissolved substance are free to move about in solution, and they are separated from one another by distances which (at least, in dilute solutions) are large compared to the diameter of the molecules. This is strikingly similar to the condition of gas molecules, the chief difference being that in a solution there is another substance surround-

[1] FLÜGEL and ROTH, *Z. physik. Chem.*, **79**, 577 (1912).

ing the solute molecules, while in a gas the intermolecular space is void. Such considerations led van't Hoff to suggest that the solute might exert an "osmotic pressure" corresponding to the pressure which it would exert as a gas if the solvent were removed. To test out this similarity it would only be necessary to find a membrane which allowed free passage of the solvent and wholly stopped the passage of the dissolved substance. A piston composed of this material could then be forced through pure solvent contained in a cylinder without encountering an opposing equilibrium pressure, but it could not force solvent out of a *solution* and compress the dissolved substance into a smaller space without overcoming the "osmotic" pressure exerted by solute molecules. If our idea of this pressure is correct, the pressure exerted on this "semipermeable" piston should be that which the solute would exert if it were a gas at the same temperature and in a volume equal to that of the solution. The pressure should increase with the temperature in the same way that the pressure of a gas increases, or in proportion to the absolute temperature. For the calculation of this pressure, the existence of solvent can be ignored, while the dissolved substance may be regarded as existing in the gaseous condition in the volume of the solution.[1]

The existence of such a pressure has been established by the use of membranes of copper ferrocyanide (among other substances) precipitated in the walls of a porous clay pot. Such a wall allows free passage of water, but retains sugar molecules. This pressure is called the "osmotic pressure" of a solute; it is due to the kinetic energy of the dissolved molecules just as the pressure of a gas is due to bombardment by its molecules; and its value is approximately equal to the pressure of a gas at the same concentration, provided this is not too large.

The osmotic pressure of a mol of solute in 1000 grams of water should be approximately that of a mol of gas confined in a liter, that is, about 25 atmospheres at room temperature. Just as the simple gas law $pv = nRT$ fails to express accurately the behavior of a gas under a pressure of 25 atmospheres, the osmotic pressure as measured is not exactly equal to the corresponding gas pressure. Osmotic-pressure data have so far been obtained for substances

[1] JAEGER, *Ann. Physik*, **54**, 463 (1918).

having quite complex molecules, owing to the difficulty of preparing membranes impermeable to the smaller molecules. The deviations of gases from the ideal gas law are always greater for complex molecules than for simpler ones and it is not surprising that this should also be true for the osmotic pressure of a solute composed of large molecules.

In spite of the experimental difficulties in connection with osmotic pressure determinations, Morse[1] and his co-workers in America and Berkley and Hartley[2] in England have prepared membranes of satisfactory impermeability to sugar, glucose, and mannite, by precipitating copper ferrocyanide or nickel ferrocyanide within the pores of clay vessels. After experiments extending over many years they were able to make these membranes of a quality suited to exact experimental work, and by means of them to measure accurately the osmotic pressures of several solutions over a range of temperature and concentration. The tables below have been taken from the final report of Morse upon this work. In the columns headed "Ratio" are given the ratios of the actual osmotic pressures measured to the calculated gas pressure. As the solutions were quite concentrated, a correction for the volume of the molecules was made by calculating the gas pressures at the volume of the solvent in the solution.

TABLE 58.—OSMOTIC PRESSURES OF MANNITE SOLUTIONS, IN ATMOSPHERES

Molal concentration	10°		20°		30°		40°	
	Osmotic pressure	Ratio	Osmotic pressure	Ratio	Osmotic pressure	Ratio	Osmotic pressure	Ratio
0.1	2.314	1.002	2.395	1.002	2.467	0.999	2.557	0.998
0.2	4.609	0.998	4.781	1.000	4.943	1.000	5.107	1.000
0.3	6.940	1.002	7.181	1.001	7.430	1.002	7.664	1.001
0.4	9.209	0.997	9.570	1.001	9.881	0.999	10.216	1.000
0.5	11.613	1.006	11.960	1.001	12.345	0.998	12.804	1.003
0.6	.....	.....	.....	.....	.....	.....	15.315	1.000

[1] *Carnegie Inst. Publ.*, **198** (1914).

[2] *Phil. Trans. Roy. Soc. London*, (*A*) **209**, 177–203 (1909); (*A*) **218**, 295 (1919).

TABLE 59.—OSMOTIC PRESSURES OF SUGAR SOLUTIONS, IN ATMOSPHERES

Molal concentration	0°		20°		40°		60°		Average ratio
	Osmotic pressure	Ratio	Osmotic pressure	Ratio	Osmotic pressure	Ratio	Osmotic pressure	Ratio	
0.1	2.462	1.106	2.590	1.130	2.560	0.998	2.717	1.000	1.06
0.2	4.723	1.065	5.064	1.060	5.163	1.012	5.438	1.001	1.03
0.4	9.443	1.060	10.137	1.060	10.599	1.037	10.866	1.000	1.04
0.6	14.381	1.077	15.388	1.071	16.146	1.053	16.535	1.015	1.05
0.8	19.476	1.091	20.905	1.093	21.806	1.068	22.327	1.025	1.07
1.0	24.826	1.130	26.638	1.130	27.701	1.085	28.367	1.045	1.10

It will be seen that the osmotic pressures of sugar solutions are uniformly higher than the calculated gas pressures, but this is not strange in view of the complexity of the molecules. Gaseous substances with large molecules deviate considerably from the laws of ideal gases, and it is not in the least remarkable that dissolved substances do the same. Osmotic-pressure determinations on simple dissolved molecules are very much needed, but the problem of finding a suitable membrane is greatly increased when smaller molecules are concerned. The results given show beyond question that there is a similarity between the behavior of a dissolved substance and that of a gaseous substance. In correspondence with fundamental law of ideal gases, we may write

$$\pi = \frac{nRT}{v} \text{ or } \pi = CRT \qquad (13)$$

as an expression of the change of osmotic pressure π with the volume and temperature of the solution. The value of R in this equation is the same as that in the gas equation. If osmotic pressure is measured in atmospheres, the volume of solvent in liters, n is the mols of solute, n/v is the molal concentration C, and R is 0.082 liter-atmosphere, just as in the gas equation.

This equation $\pi = CRT$ might also be used to determine molecular weights in solution from measured osmotic pressures. If m grams of solute having a molecular weight M are present in v liters of solvent,

$$\pi = \frac{mRT}{Mv}$$

and M is readily calculated. Osmotic-pressure measurements are so difficult, from an experimental point of view, that molecu-

lar weights are seldom so determined. Boiling-point elevations or freezing-point depressions lead to the same molecular weights, and are far more easily carried out in the laboratory.

It will be recalled that we have developed a relation between the boiling-point elevation of a solution and the mol fraction of solute by means of Raoult's law, which takes account of the vapor-pressure lowering produced by the solute; and that a similar equation was developed for the freezing-point depression. There is also an equation connecting the osmotic pressure of a solution with the vapor pressure of solvent above it. This equation is

$$\pi = \frac{RT}{v_l} ln \frac{p_0}{p}, \tag{14}$$

where v_l is the volume of 1 mol of pure liquid solvent, p_0 is the vapor pressure of pure solvent, and p the vapor pressure of solvent from the solution.[1] For dilute solutions this equation

[1] Equation (14) may be derived by considering a cycle in which (*a*) a mol of solvent is expressed reversibly from a very large quantity of solution by the motion of an osmotic piston into it; (*b*) this mol of solvent is vaporized reversibly under its own vapor pressure; (*c*) the vapor is expanded reversibly until its pressure is equal to that of solvent above the solution; and (*d*) the vapor is condensed reversibly into solution again. The work done upon the system when a mol of solvent is expressed from the solution by a semipermeable piston is πv_l, or the work done by the system is

$$w = -\pi v_l. \tag{a}$$

When a mol of solvent evaporates under its vapor pressure p_0, the work done by the system is

$$w = p_0(v_v - v_l). \tag{b}$$

If we consider the vapor as an ideal gas, $p_0 v_v$ is RT; and v_l is negligible in comparison with v_v, so that $w = RT$. When the vapor expands reversibly from p_0 to p, the work done by the system is $w = \int p dv$ To integrate this equation we must express pressure as a function of the vapor volume, which may be done by writing $p = RT/v$. Hence

$$w = RT\ ln(v_2/v_1), \tag{c}$$

where v_2 is the molal volume corresponding to p and v_1 corresponds to p_0. Since $pv_2 = p_0 v_1$ we may write for this step $w = RTln(p_0/p)$. Next condense the vapor into solution under the constant pressure p. In this step the work done by the system is $p(v_l - v_v)$, which is substantially $-RT$, that is,

$$w = -RT. \tag{d}$$

The sum of all of the above work terms is

$$RT + RTln(p_0/p) - RT - \pi v_l,$$

and this must be zero for a reversible isothermal cycle as required by the

reduces to equation (13) above when the vapor pressures are in agreement with those calculated from Raoult's law. For concentrated solutions p must be measured experimentally.

When osmotic pressures of strong solutions are calculated from equation (13), they do not agree with the results of experiment, and the deviations are serious. They are doubtless due in part to combination of solute and solvent (hydration), and to molecular association of the solvent. These same factors would lead to lower vapor pressures than those demanded by Raoult's law. But if the measured vapor pressure is substituted in equation (14), a calculated osmotic pressure in substantial agreement with the experimental one is obtained. This is illustrated in Table 60, where it will be seen that equation (14) represents the experimental data satisfactorily.

TABLE 60.—CANE SUGAR SOLUTIONS AT 30°

Molal concentration	Measured osmotic pressure[1] (atmospheres)	Calculated osmotic pressures			
		Equation (13)	Per cent error	Equation[2] (14)	Per cent error
0.10	2.47	2.47	0	2.47	0.0
1.00	27.22	24.72	9	27.0	1.0
2.00	58.37	49.40	15	58.4	0.0
3.00	95.16	74.20	23	96.2	0.0
4.00	138.96	98.90	29	138.3	0.5
5.00	187.3	123.60	33	182.5	2.5
6.00	232.3	148.30	36	230.9	0.6

[1] FRASER and MYRICK, *J. Am. Chem. Soc.*, **38,** 1907 (1916).

[2] Vapor pressures from BERKLEY, HARTLEY, and BURTON, *Phil. Trans. Roy. Soc. London*, **218,** 295 (1919). The data for round concentrations are as follows:

Molal concentration	1.00	2.00	3.00	4.00	5.00	6.00
Ratio p_0/p	1.020	1.044	1.072	1.104	1.140	1.177

second law of thermodynamics. Equating this sum to zero and solving for πv_l, we find

$$\pi v_l = RT ln(p_0/p),$$

which is equation (14) on p. 161.

A symposium on osmotic pressure, presenting various points of view of prominent investigators, will be found in *Trans. Faraday Soc.*, **13,** 119–189 (1917). Reference should also be made to the "Monograph on Osmotic Pressure" by ALEXANDER FINDLAY (1913), where additional information will be found.

Questions

1. The vapor pressure of acetic acid at 50° is 55 mm., that of benzol is 267 mm. Calculate the partial pressure of each from a solution in which the mol fraction of the acid is 0.30, and calculate the total vapor pressure. The measured total pressure is 236 mm. Calculate the per cent deviation.

2. The vapor pressure of CCl_4 at 50° is 308 mm., that of benzol is 267 mm. Calculate the total vapor pressure of a solution of 1 mol of CCl_4 in 3 mols of benzol. The observed pressure is 185 mm. What is the per cent error in the calculated pressure?

3. Steam is passed through a mixture of nitrobenzene and water, which are *not soluble in one another*, and the distillate is caught in a graduate. When the total volume of distillate is 100 c.c. the nitrobenzene layer is 13 c.c. What is the partial pressure of each substance in the vapor in the distilling flask, if the total pressure is 1 atmosphere? What is the temperature of the distillation? The vapor pressure of water changes 27 mm. per degree; the density of nitrobenzene ($C_6H_5NO_2$) is 1.20.

4. At 18° a liter of water dissolves a liter of CO_2 when the pressure of CO_2 is 1 atmosphere. Calculate the molal concentration in a solution over which the partial pressure of CO_2 is 150 mm.

5. From the data of Table 29 calculate the molal boiling-point constants for ether and for ethyl alcohol, and compare them with those of Table 53.

6. Calculate the latent heat of evaporation of stannic chloride from its molal boiling-point constant.

7. Carbon disulfide boils at 46°, its latent heat is 84 cal. per gram. Calculate its boiling-point constant. A solution of 25 grams of sulfur in 1000 grams of CS_2 boils at 46.24°. Calculate the molecular weight of dissolved sulfur.

8. A solution of 3.17 grams of anthracene (mol weight 178) in 100 grams of benzene boils 0.50° higher than pure benzene. Calculate the latent heat of evaporation of benzene.

9. Benzene (C_6H_6) freezes at 5.42° and boils at 80°. Its heat of vaporization at the boiling point is 95.46 cal. per gram. A solution of 12.8 grams of naphthalene ($C_{10}H_8$) in 1000 grams of benzene freezes at 4.918°. (*a*) At what temperature will this solution boil? (*b*) What will be the vapor pressure of benzene above this solution at 80°? How many calories are absorbed during the melting of a gram of benzene? What is the vapor pressure of pure benzene at 70°?

10. The vapor pressure of CH_3OH at its boiling point, 66°, changes 17.7 mm. per degree. Calculate the boiling point of a solution containing 2 grams of a non-volatile solute of molecular weight 65 in 96 grams of methyl alcohol.

11. Naphthalene ($C_{10}H_8$) melts at 80.05°, and a solution containing 9.21 per cent by weight of phthalic anhydride is in equilibrium with solid naphthalene at 75.1°. Calculate the molecular weight of phthalic anhydride.

12. Phthalic anhydride ($C_6H_4(CO)_2O$) melts at 130.84°, and a solution containing 8.30 per cent by weight of naphthalene is in equilibrium with solid anhydride at 124.8°. (*a*) Given the molecular weights of both substances, calculate the latent heat of fusion of a mol of phthalic anhydride, and the freezing-point constant F. (*b*) Calculate the freezing point of a solution of 4 mols of phthalic anhydride and 1 mol of naphthalene. The observed freezing point of this solution is 118°.

13. A solution containing 29 per cent by weight of phthalic anhydride is in equilibrium with both solid naphthalene and solid phthalic anhydride at a certain temperature. Calculate the freezing point from equation (10), first considering naphthalene as the solvent, then phthalic anhydride as the solvent. The observed freezing point is 65°. Calculate the error which results from applying the freezing-point equation for dilute solutions to a solution which is obviously not dilute.

14. A solution of 0.60 gram of acetic acid in 50 grams of water freezes at −0.375°. Calculate the molal freezing-point constant F for water. Calculate the molecular weight of a solute 68 grams of which in 1000 grams of water lowers the freezing point 0.469°.

15. The vapor pressure of a solution of 2.38 mols of cane sugar ($C_{12}H_{22}O_{11}$) in 1000 grams of water at 30° is 94.88 per cent that of pure water. Calculate the osmotic pressure of this solution from the vapor pressure. Calculate also its osmotic pressure assuming that it behaves as an ideal gas at this concentration. The measured osmotic pressure is 73 atmospheres.

16. Make the same calculations as in the previous problem for a solution of 5.35 mols of sugar per 1000 grams of water, where the vapor pressure is lowered 13.24 per cent, and calculate the percentage deviation from the measured osmotic pressure, 180 atmospheres at 30°.

17. A mixture of H_2O and chlorbenzol (C_6H_5Cl), which are not soluble in one another, is distilled with steam at 1 atmosphere. The distillate is 71 per cent by weight of chlorbenzol. (*a*) Calculate the partial pressure of each substance in the vapor. (*b*) Calculate the temperature of distillation. The vapor pressure of water is 525 mm. at 90°, 588 mm. at 93°, 657 mm. at 96°.

18. At 75° the vapor pressure of benzene (C_6H_6) above a solution of 9 grams of naphthalene ($C_{10}H_8$) in 100 grams of benzene is 607 mm. The latent heat of evaporation of benzene is 7450 cal. per mol. (*a*) Calculate the vapor pressure of pure benzene at 75°. (*b*) Calculate the boiling point of pure benzene. (*c*) Calculate the boiling point of the solution.

19. Naphthalene ($C_{10}H_8$) melts at 80°; a solution containing 1 per cent by weight of nitrobenzene ($C_6H_5NO_2$) freezes at 79.43. Calculate the freezing-point constant of naphthalene. Calculate the latent heat of fusion of naphthalene.

20. Chloroform ($CHCl_3$) boils at 60.2° and has a vapor pressure of 781 mm. at 61°. (*a*) Calculate the vapor pressure at 60.2° of a solution containing 0.2 mol of non-volatile solute in 1000 grams of chloroform. (*b*) Calculate the boiling point of the solution. (*c*) Calculate the boiling-point constant for chloroform. (*d*) Calculate the latent heat of evaporation per mol of chloroform.

21. Mixtures of propyl alcohol (C_3H_7OH) and water are distilled and analysis of the distillate made by determining the boiling point of the distillate. Draw a boiling-point-composition diagram. Show the form of vapor-pressure-composition diagram for 90°, and indicate the position of the vapor line. Draw a line showing $p = 760$ on this diagram.

Per cent alcohol in the mixture.....	20	40	60	80	100
Boiling point of mixture.....	92	88	86	87	97
Boiling point of distillate.....	87	86.2	86	86.5	

22. The vapor pressure of water changes 27 mm. per degree at 100°. The vapor pressure of butyric acid ($C_4H_9CO_2H$) is 45 mm. at 100°, and it changes 3 mm. per degree. The density of butyric acid is 0.96, and it is insoluble in water. (*a*) Calculate the temperature at which it will distil with steam. (*b*) Calculate the ratio of volume of butyric acid to water in the distillate.

23. The vapor pressure of water at 20° is 17.406 mm., that of a solution of 144 grams of mannite ($C_6H_{14}O_6$) in 1000 grams of water is 17.158. (*a*) Calculate the mol fraction of mannite in solution from the vapor-pressure lowering. (*b*) The heat of fusion of ice is 79 cal. per gram. Calculate the freezing point of the solution. (*c*) Calculate the molecular weight of mannite.

24. Pure *A* boils at 90° and *B* has at 90° a vapor pressure of 500 mm. A mixture of 75 mol per cent of *A* has a vapor pressure of 800 mm. at 90° and gives on boiling at atmospheric pressure a first distillation richer in *B*. Sketch the boiling-point diagram for atmospheric pressure. What final products result from repeated fractionization of 80 mol per cent of *A*? 10 mol per cent of *A*?

25. The vapor pressure of ammonia is 11.65 meters of mercury at 40° and 19.61 meters at 60°. Calculate the latent heat of vaporization of a mol of ammonia.

26. The latent heat of evaporation of ether ($C_4H_{10}O$) is 85 cal. per gram at its boiling point, 35°. A solution composed of 2.60 grams of solute in 100 grams of ether boils at 36.10°. Calculate the molecular weight of the solute.

27. Ethyl alcohol has at 15° a vapor pressure of 32.18 mm., and that of an alcoholic solution of a solute of molecular weight 210 has at the same temperature a vapor pressure of 31.98 mm. How many grams of solute are there per 100 grams of solvent?

28. The heat of vaporization of water at 100° is 537 cal. per gram. A solution of glycerol ($C_3H_8O_3$) in water boils at 101.545°. Calculate the molal concentration of the glycerol in water.

29. A liquid of density 1.20 and insoluble in water is distilled with steam at a total pressure of 760 mm., and the distillation temperature is 99.25°. The distillate consists of 6.7 c.c. of water for each cubic centimeter of the other liquid. The vapor pressure of water changes 27.2 mm. per degree. Calculate the molecular weight of the substance in the vapor state.

30. When 2.83 grams of solute are dissolved in 100 grams of alcohol at 15°, the vapor pressure of the solvent changes from 32.18 to 31.98 mm. Calculate the molecular weight of the substance dissolved.

31. Chloroform ($CHCl_3$) and acetone (C_2H_6O) form a maximum boiling mixture containing 35 mol per cent of acetone. A kilogram of solution containing 25 mol per cent of chloroform is separated into two portions by repeated fractional distillation. State the composition in mol per cent and calculate the weight in grams of each of the two portions.

32. Benzene (C_6H_6) melts at 5.00°C. and its freezing-point constant F' is 65.4. A solution containing 6.25 per cent of lubricating oil in benzene freezes at 3.00°C. (*a*) Calculate the molecular weight of the lubricating oil. (*b*) Calculate the heat of fusion per gram of benzene. (*c*) Calculate the molal freezing-point constant F of benzene.

33. The distribution ratio of formaldehyde (HCOH) between water and ether is 9.2. (*a*) How many cubic centimeters of water will be necessary to remove in one extraction 95 per cent of the formaldehyde from a liter of ether solution containing 1 mol of formaldehyde? (*b*) How much formaldehyde would be left in a molal solution in ether after two consecutive extractions made with 50-c.c. portions of water?

34. Chlorine boils at −23°C. and its molal latent heat is 1330 cal. (*a*) Calculate the vapor pressure at −23°C. of a solution made from 1000 grams of liquid chlorine and 12.7 grams of iodine. There forms a compound (ICl_3), which is not volatile. (*b*) Calculate the boiling point of this solution.

35. The solubility of ammonia in chloroform is 0.091 mol per liter when the partial pressure of NH_3 above the solution is 760 mm. and the distribution ratio between $CHCl_3$ and water is 0.040. (*a*) Calculate the resulting concentrations when a liter of this solution is shaken with 100 c.c. of water. (*b*) Calculate the pressure of ammonia above the water layer.

36. The solubility of gases is often tabulated as the "Bunsen coefficient," α, which is the cubic centimeters of gas (measured at 0° and 760 mm.) dissolved per cubic centimeter of solvent at the temperature in question when the partial pressure of the gas is 760 mm. This coefficient has the following values for CO_2 dissolved in water:

t	0°	10°	20°	30°
α	1.713	1.194	0.878	0.665

Calculate the molal solubility corresponding to some of these figures.

37. Another common way of reporting solubility data is as grams of gas per 100 grams of solvent when the *total* pressure (of solvent plus solute) is 1 atmosphere. This coefficient q has the following values for Cl_2 dissolving in water:

t	10°	20°	30°	50°
q	0.997	0.729	0.572	0.393

(*a*) Calculate a rough value of each solubility. (*b*) Estimate the partial pressure of solvent for each temperature from Raoult's law and the data on page 77. (*c*) Assuming Henry's law to hold over a small range of solute pressure, calculate the solubility in mols per 1000 grams of water when the *partial pressure of chlorine* is 1 atmosphere.

CHAPTER VI

SOLUTIONS OF IONIZED SOLUTES

There is a class of solutions to which the laws developed in the previous chapter do not apply without considerable alteration. This includes solutions of practically all inorganic substances in water, in anhydrous formic acid, in liquid ammonia, and some other solvents. The vapor pressure, freezing point, boiling point, and osmotic pressure of these solutions, when used to calculate the mol fractions of solutes, lead to numbers inconsistent with the smallest possible molecular weights. It was also found that such solutions conduct electricity quite well, while ideal solutions which conform to the simple laws given in the previous chapter do not conduct electricity to any considerable extent. These facts led Arrhenius to suggest that the solutes are dissociated in solution into electrically charged parts of molecules, called ions. The early experimental work of Arrhenius, Ostwald, van't Hoff, and Hittorf has been continued by others, and as data were accumulated a fairly comprehensive theory developed. By means of a few simple assumptions it seemed possible to account for the behavior of ionized solutes in dilute solutions "within the experimental error." There were, however, certain facts for which the fundamental assumptions offered no explanation and which, indeed, showed that the assumptions themselves were not entirely correct. This was early recognized by some writers,[1] but was ignored by most of the advocates of the ionic theory. As data of high accuracy became available in quantity, it was more and more evident that the commonly accepted theory must be revised. Recent activity along these lines makes it seem probable that the theory of electrolytic solutes will undergo extensive revision within the next few years. In view of this probability it seems best to present the material of this chapter in the following order:

[1] Lewis, *Z. physik. Chem.*, **70**, 212 (1909).

(*a*) A statement of the experimental *facts* which have now been accumulated and which any satisfactory theory must explain quantitatively.

(*b*) A brief outline of the original theory, of the assumption on which it was based, and of the experimental facts with which it is and is not in accord.

(*c*) A brief account of some of the newer developments.

Types of Electrolytes.—Ionizing substances may be divided into classes according to their products upon ionization. Simple binary (or uni-univalent) electrolytes are those such as hydrochloric acid, sodium nitrate, and potassium acetate, which yield a single positive ion bearing a unit charge, and a single negative ion bearing a unit charge for each molecule ionized. Substances of this type exhibit the simplest phenomena in solution, and they have been more studied than salts of other types. Another simple type of ionization is that exhibited by copper sulfate and other salts similar to it; each ion bears two units of electricity upon it, but a molecule forms only two ions. The remaining types of ionized solutes are more puzzling in their behavior, and more difficult to study experimentally, on account of the possibility of ionization in different ways or in different steps. Thus sulfuric acid may ionize according to the reaction[1]

$$H_2SO_4 = H^+ + HSO_4^-$$

and the negative ion may ionize further

$$HSO_4^- = H^+ + SO_4^{--}.$$

The formation of intermediate ions of the HSO_4^- type is very common in the ionization of weak acids such as H_2CO_3 or H_2SO_3. It is also possible for salts like barium chloride to ionize according to the scheme

$$BaCl_2 = BaCl^+ + Cl^-.$$

No satisfactory general methods have been devised for establishing definitely the presence or absence of these intermediate ions in the case of salts, but some evidence of their existence will be discussed later.[2]

[1] Noyes and Stewart, *J. Am. Chem. Soc.*, **32**, 1133 (1910)

[2] Experiments in which the chlorides of Ba, Sr, Ca, Zn, Cd, Mn, Co, Mg, Ni, or Cu were shaken with ammonium permutite to equilibrium

Vapor-pressure Lowering for Ionized Substances.—In Table 61 are shown the vapor-pressure lowerings for solutions of potassium chloride[1] together with the vapor-pressure lowering for mannite solutions of the same concentration. Upon dividing the figures in the second column by those in the third, a value is obtained which is called the "mol number," shown in the fourth column. This is the number by which the effect expected from an ideal non-ionized solute must be multiplied to obtain the observed effect. It was designated as "i" by van't Hoff and is frequently called "van't Hoff's i." It will be called the mol number in this book.

TABLE 61.—VAPOR PRESSURE OF POTASSIUM CHLORIDE SOLUTIONS AT 20° COMPARED WITH MANNITE SOLUTIONS

Formal concentration	$p_0 - p$ for KCl	$p_0 - p$ for mannite	Mol number
0.05	0.0294	0.0156	1.885
0.10	0.0574	0.0311	1.846
0.20	0.1128	0.0622	1.814
0.30	0.1680	0.0934	1.799
0.40	0.2225	0.1243	1.790
0.50	0.2785	0.1555	1.790

Osmotic Pressures of Ionized Solutes.—On account of the difficulty of preparing membranes impermeable to dissolved salts, few determinations of the osmotic pressure of ionized solutes have been made; but these experiments[2] lead to about the same mol numbers as are obtained from vapor-pressure or freezing-point experiments. The results for lithium chloride are

indicate that no ions of the type MCl^+ exist below normal concentrations. (GUNTHER-SCHULZE, *Z. Elektrochem.*, **28**, 387 (1922).) On the other hand, transference data for concentrated solutions of cadmium chloride are difficult to interpret unless $CdCl^+$ ions exist in solution, and experiments upon the behavior of sulfuric acid (NOYES and STEWART, *J. Am. Chem. Soc.*, **32**, 1133 (1910)) seem to indicate definitely the presence of HSO_4^- ions in solution.

[1] LOVELACE, FRASER, and SEASE, *J. Am. Chem. Soc*, **43**, 119 (1921).

[2] MORSE, *Carnegie Inst. Pub.*, **198**, 217 (1914).

shown in Table 62 in which the last line gives the ratio of the observed pressure to that expected from an ideal solute. This is, therefore, the mol number.

TABLE 62.—OSMOTIC PRESSURES OF LITHIUM CHLORIDE AT 30°

Concentration of salt, mols per 1000 grams of water	0.10	0.20	0.30	0.40	0.50
Observed osmotic pressures	4.317	8.976	13.768	18.772	24.162
Calculated gas pressure for undissociated salt	2.472	4.943	7.415	9.866	12.358
Ratio osmotic pressure to ideal gas pressure (or mol number i)	1.746	1.816	1.857	1.955	1.992

Freezing Points of Ionized Solutes.—Data are available in much larger quantities upon the freezing-point depressions produced by salts; those in Table 63 may be taken as typical of modern work of high quality. It will be noted that the figures in the third column are very much larger than 1.86,° which is the freezing-point depression per mol of solute to be expected in the ideal solution. Upon dividing these figures by 1.86 we obtain the mol numbers shown in the fourth column. In connection with these data, as well as those for vapor pressure and osmotic pressure, it should be noted that the mol number changes with the concentration, and also that the mol numbers for different salts at the same concentration are not exactly the same. This difference is particularly noticeable when salts of different types, such as potassium nitrate and magnesium sulfate, are compared.

An examination of available data upon freezing points[1] of salts in aqueous solution shows that salts of the same type have nearly the same mol numbers at a given concentration. Thus for salts of the KCl type (giving one positive ion and one negative ion) the maximum and minimum mol numbers for 0.1 formal were 1.875 and 1.856. Some of the data for other salts are shown in Table 64.

[1] NOYES and FALK, *J. Am. Chem. Soc.*, **32**, 1011 (1910).

TABLE 63.—FREEZING-POINT LOWERINGS AND MOL NUMBERS

Formal concentration	Freezing-point lowering	Lowering per formula weight	Mols of solute per formula weight of salt
Potassium nitrate[1]			
0.002	0.00731	3.655	1.967
0.005	0.01819	3.638	1.958
0.010	0.03599	3.599	1.937
0.020	0.07088	3.544	1.908
0.050	0.17150	3.431	1.848
0.100	0.33140	3.314	1.787
Potassium chloride[1]			
0.002	0.007316	3.658	1.969
0.005	0.01822	3.643	1.961
0.010	0.03609	3.609	1.943
0.020	0.07140	3.570	1.922
0.050	0.1752	3.505	1.888
0.100	0.3451	3.451	1.861
Sodium bromate[2]			
0.001	0.003689	3.689	1.985
0.002	0.007365	3.683	1.980
0.005	0.01828	3.656	1.967
0.010	0.03607	3.607	1.940
0.020	0.07134	3.567	1.913
0.050	0.1742	3.485	1.875
0.100	0.3409	3.409	1.835
Magnesium sulfate[3]			
0.005	0.01588	3.175	1.708
0.010	0.0300	3.000	1.614
0.020	0.0565	2.825	1.520
0.050	0.1294	2.589	1.394
0.100	0.2420	2.420	1.303
0.200	0.4504	2.252	1.214
0.500	1.0180	2.036	1.099

[1] ADAMS, *J. Am. Chem. Soc.*, **37**, 495 (1915).
[2] FLUGEL and ROTH, *Z. physik. Chem.*, **79**, 557 (1912).
[3] HALL and HARKINS, *J. Am. Chem. Soc.*, **38**, 2672 (1916).

TABLE 64.—MOL NUMBERS DERIVED FROM FREEZING-POINT LOWERINGS

Substance	Concentration								
	0.005	0.01	0.02	0.05	0.1	0.2	0.3	0.4	0.5
KCl	1.963	1.943	1.918	1.885	1.861	1.833	1.818	1.808	1.800
NaCl	1.953	1.938	1.922	1.892	1.875	1.850	1.838	1.830	1.824
LiCl	1.944	1.937	1.928	1.912	1.901				
$NaNO_3$	.....	1.903	1.885	1.855	1.830	1.798			
KOH	1.995	1.983	1.967	1.926	1.865				
HCl	1.991	1.975	1.957	1.933	1.917				
HNO_3	1.974	1.960	1.942	1.912	1.900	1.879			
K_2SO_4	2.857	2.798	2.713	2.570	2.459	2.333	2.248	2.186	2.136
$BaCl_2$	2.797	2.756	2.709	2.637	2.575	2.515	2.479		
$ZnCl_2$	2.913	2.845	2.771	2.666	2.579	2.493			
H_2SO_4	2.719	2.591	2.467	2.316	2.216	2.125	2.080	2.047	2.022
$MgSO_4$	1.694	1.618	1.536	1.420	1.324	1.223	1.162	1.119	1.084
$CuSO_4$	1.616	1.545	1.455	1.318					

Mol Numbers and Boiling Points.—Since the depression of a freezing point and the elevation of a boiling point are both due to a change in the vapor pressure of solvent following a decrease in its mol fraction, it will be seen that boiling-point elevations might be expected to yield mol numbers similar to those already given. However, since the molal boiling-point elevation for water is 0.518° and the molal freezing-point depression is 1.86°, the latter is a more suitable method of measuring mol numbers. It so happens that the mol numbers vary but little with the temperature, but there is a slight decrease at higher temperatures. The following data are for solutions of silver nitrate:

TABLE 65.—BOILING POINTS OF SILVER NITRATE SOLUTIONS

Grams per 1000 grams water	Elevation of boiling point	Elevation per formula weight	Mol number
8.04	0.044	0.93	1.82
38.9	0.197	0.86	1.69
74.9	0.382	0.87	1.70
155.5	0.741	0.81	1.59
350.8	1.526	0.74	1.45

Landolt-Börnstein Tables, p. 1461.

Conduction of Electricity.—Solutions which have the properties discussed above also conduct electricity; those which do not show these deviations from the molal properties of ideal solutions do not conduct. On account of this property of conducting electricity, the substances which ionize in solution are often called "electrolytes." There is one fundamental difference between the conduction of these solutions and that of the metals. Metallic conduction is not accompanied by the movement of matter, while *electrolytic conduction* is accompanied by the movement of matter. Thus when copper chloride solution is placed between two inert electrodes, copper is deposited upon the negative one and chlorine is evolved from the positive electrode. Decomposition of a dissolved substance into two portions which appear at different places is called *electrolysis;* metallic conductors through which electricity enters and leaves the solution are the *electrodes.* We shall consider three distinct steps in connection with the passage of electricity through solution, though it is understood that these three steps actually occur simultaneously. (*a*) There is a chemical reaction by which electricity passes from electrode to the solution; (*b*) there is a transfer of charged particles of matter through the solution in opposite directions; and (*c*) another chemical reaction by which electricity passes from the solution to the second electrode and out of solution. These chemical changes will be considered first.

Faraday's Law of Electrolysis.—Consider four solutions containing electrodes as follows: (*a*) sodium chloride solution, with a carbon anode and a platinum cathode; (*b*) sodium chloride solution, with a zinc anode and a silver-chloride-coated cathode; (*c*) silver nitrate solution with a platinum anode and a platinum cathode; (*d*) copper sulfate with a platinum anode and platinum cathode; and let these four cells be connected in series so that the positive electrode of the second is connected to the negative of the first, and so on, as shown in Fig. 40. If a current of electricity is passed through these cells, the products of electrolysis will appear as deposits upon the electrodes, as gases evolved from solution, or as new solutes in solution near the electrodes, as follows: (*a*) chlorine is evolved from the carbon anode, hydrogen is evolved from the platinum cathode, and sodium hydroxide is formed in the solution around it; (*b*) zinc chloride is formed in

solution around the zinc anode, silver chloride is reduced to silver at the cathode, and sodium chloride is formed around this electrode; (*c*) oxygen is evolved from the platinum anode, nitric acid forms around it, and silver is deposited upon the platinum cathode; (*d*) oxygen is evolved from the anode, sulfuric acid is formed in solution near it, and copper is deposited upon the cathode.

The solutions are not assumed to be of the same strength, or at the same temperature, or of the same resistance; the only condition imposed is that all of the electricity which passes through one cell must also pass through the others. A quantitative examination of the products of electrolysis will show that the sulfuric acid formed at the anode in *d* is just sufficient to neutralize the sodium hydroxide formed at the cathode in *a*: that the chlorine evolved from the anode in *a* will convert all of the silver deposited on the cathode in *c* into silver chloride;

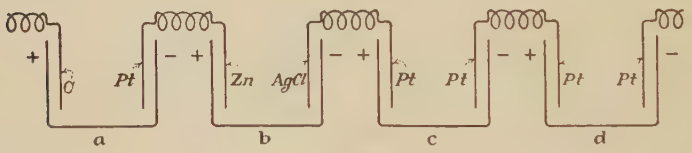


FIG. 40.

or all of the copper on the cathode from *d* into copper chloride; that the silver formed from silver chloride in *b* is equal in weight to that deposited in *c*; the sodium hydroxide of *a* will precipitate all of the zinc chloride formed at the anode in *b* as zinc hydroxide; and that, if this is ignited to zinc oxide, the oxide so formed is just sufficient to react with the sulfuric acid of *d*. In other words, the substances produced at the electrodes during electrolysis are chemically equivalent to one another. Upon passing twice as much electricity through the solutions, twice as much of each product is formed; these two statements together constitute Faraday's law: The quantity of chemical action produced at *each electrode* by the passage of electricity is strictly proportional to the quantity of electricity, and dependent upon that alone; and in such electrolysis chemically equivalent quantities of substance are produced at the electrodes.

Faraday's law is absolutely exact under all conditions; no exceptions to it are known, and on it is based the definition of unit current. A current of 1 ampere is that current which will deposit in 1 sec. from a solution of silver nitrate 0.0011180 gram of silver. This quantity of electricity is called an ampere-second or one coulomb. It is of interest to compute the quantity of electricity necessary to deposit one chemical equivalent, or one atomic weight of silver, since this is the quantity of electricity which will deposit one equivalent of any other substance from solution. The desired figure is 107.880/0.0011180 = **96,500 coulombs.** This quantity of electricity is called **one faraday** of electricity, after the name of Faraday, the discoverer of the law. We may now state this important law again in the form: The passage of 1 faraday of electricity through a solution will cause the reaction of one chemical equivalent of some substance at *each electrode.* It is important to note that chemical action is required to pass electricity into a solution, and further action to pass it out again, so that one equivalent of electrolytic product is formed at *each* electrode.

Much experimental work has been done[1] on the electrolysis of silver nitrate solutions in connection with the definition of the international ampere, particularly by our own Bureau of Standards and the English National Physical Laboratory. An interesting confirmation of Faraday's law was obtained[2] by depositing silver in the standard instrument (called a coulometer), while in the same circuit iodine was liberated by the electrolysis of a solution of potassium iodide. The ratio of the weight of silver deposited to that of iodine liberated was 1:1.1762, as shown in Table 66.

The same ratio has been used by many investigators to determine the ratio of the atomic weights of these elements. An average of the ratios so obtained by very careful gravimetric work[3] is 1.1763, which agrees with the electrochemical ratio

[1] *Bull. Bur. Standards,* **1,** 1 (1904); **9,** 494 (1912); **10,** 425; **11,** 220, 555 (1914); *Sci. Paper,* **283** (1916); Richards, *Proc. Am. Acad. Arts Sci.,* **37,** 415 (1902); **44,** 91 (1908); *J. Am. Chem. Soc.,* **37,** 692 (1915); Smith, Mather, and Lowry, *Res. Nat. Phys. Lab.,* **4,** 125.

[2] Bates and Vinal, *J. Am. Chem. Soc.,* **36,** 916 (1914); *Bull. Bur. Stand, ards,* **10,** 425 (1914).

[3] Clarke, *Smithsonian Misc. Coll.,* **54,** [3,] 99 (1910).

TABLE 66.—DATA ILLUSTRATING FARADAY'S LAW

Weight of silver deposited	Weight of iodine deposited	Calculated coulombs		Difference in per cent	Milligrams of iodine per coulomb	Value of the faraday (I = 126.92)
		From silver coulometer	From potential and resistance			
4.10469	4.82862	3,671.45	3,671.53	0.0002	1.31518	96,504
4.09903	4.82224	3,666.39	3,666.55	0.0004	1.31526	96,498
4.10523	4.82851	3,671.94	3,671.84	0.0003	1.31498	96,518
4.10475	4.82860	3,671.51	3,671.61	0.0003	1.31515	96,506
4.10027	4.82247	3,667.50	3,667.65	0.0004	1.31492	96,523
4.10516	4.82844	3,671.88	3,671.82	0.0001	1.31498	96,519

Average value of the faraday: **96,515**

1 : 1.1762 within 1 part in 10,000. Faraday's law is, therefore, an *exact* law of nature; it does not deviate in strong solutions like Raoult's law, it is exact at all temperatures,[1] and in all solvents.[2] In a mixture of dissolved substances, if several chemical actions occur at one electrode, the sum of the equivalents liberated in all the various reactions is exactly that required by Faraday's law. This law does not state what substance will deposit first from solution, or whether a mixture separates or not, but only that the products separating at two electrodes in the same circuit shall be chemically equivalent.[3]

Chemical Reactions at the Electrodes.—It has been stated above that Faraday's law says nothing about which of several possible reactions will occur at any electrode, but governs only the total quantity of chemical action there produced. The *electrical potential* (Chapter XVI) determines which reaction occurs, and the reaction which will occur with the smallest

[1] RICHARDS and STULL, *Proc. Am. Acad. Arts Sci.*, **38,** 409 (1902). Silver was deposited from an aqueous solution of silver nitrate at 20° and in the same circuit from silver nitrate dissolved in fused sodium nitrate and potassium nitrate at 250°. The weights of silver deposited agreed within 1 part in 20,000.

[2] KAHLENBERG, *J. Phys. Chem.*, **4,** 349 (1900).

[3] For other experiments confirming Faraday's law, see FISCHER and THIELE, *Z. anorg. Chem.*, **67,** 302 (1910); BETTS and KERN, *Electrician*, **54,** 16 (1904); EISENREICH, *Z. physik. Chem.*, **76,** 643 (1910); CARHART, *Trans. Am. Electrochem. Soc.*, **9,** 375 (1906); HULETT and VINAL, *Bull. Bur. Standards*, **11,** 553 (1914); SMITH, MATHER, and LOWRY, *Phil. Trans. Roy. Soc. London*, **207,** 545 (1908); ROSA, VINAL, and MCDANIEL, *Bull. Bur. Standards*, **9,** 209 (1913); JAEGER and v. STEINWEHR, *Z. Instrumentenk.*, **28,** 327, 353 (1908).

applied potential always takes place first. For instance, in cell *a* of Fig. 40, hydrogen was evolved at the cathode, and no sodium was deposited. Reference to the electromotive series of elements in an inorganic chemistry text, or the potentials in Table 126 will show that sodium is near the top of the list, while hydrogen is well down in it. Quantitatively, the potential required to deposit sodium is nearly 3 volts higher than that required to discharge hydrogen ions. As some hydrogen ions are present from the slight ionization of water, these are therefore discharged and the required potential for sodium is never reached. Similarly in *b*, the potential required to discharge chlorine at the zinc anode is 2 volts higher than that required for zinc to pass into solution. *The reaction requiring the lowest potential always takes place first.* There are, of course, hydrogen ions from water in the silver nitrate solution of *c*, but the potential required to discharge them is higher than that required for silver by about 0.8 volt; and the metal therefore deposits. In *a*, chlorine is evolved at the anode in place of oxygen from the hydroxide ions of water, because chlorine has a lower discharge potential than oxygen. The actual potential also depends upon the concentration in a way to be discussed later in Chapter XVI.

The *electrode reactions* discussed above may be described by chemical equations in which the electricity is written as one of the reacting substances. Thus, the electrode reactions mentioned in the paragraph on Faraday's law may be written with the sign $\oplus$ to represent 1 faraday of positive electricity as follows:

$$\left.\begin{aligned} Cl^- + \oplus &= \tfrac{1}{2}Cl_2 \\ H_2O &= OH^- + \tfrac{1}{2}H_2 + \oplus \end{aligned}\right\} \quad (a)$$

$$\left.\begin{aligned} \tfrac{1}{2}Zn + \oplus &= \tfrac{1}{2}Zn^{++} \\ AgCl &= Ag + Cl^- + \oplus \end{aligned}\right\} \quad (b)$$

$$\left.\begin{aligned} \tfrac{1}{2}H_2O + \oplus &= H^+ + \tfrac{1}{4}O_2 \\ Ag^+ &= Ag + \oplus \end{aligned}\right\} \quad (c)$$

$$\left.\begin{aligned} \tfrac{1}{2}H_2O + \oplus &= H^+ + \tfrac{1}{4}O_2 \\ \tfrac{1}{2}Cu^{++} &= \tfrac{1}{2}Cu + \oplus \end{aligned}\right\} \quad (d)$$

There is difference of custom in writing these reactions; some writers prefer to use the negative electron in the equations, since it may be lost or taken up, while a positive charge unattached

to matter has not been discovered. Following this custom the above reactions would be written

$$\left.\begin{array}{l} Cl^- = \tfrac{1}{2}Cl_2 + \ominus \\ H_2O + \ominus = OH^- + \tfrac{1}{2}H_2 \end{array}\right\} \quad (a)$$

$$\left.\begin{array}{l} \tfrac{1}{2}Zn = \tfrac{1}{2}Zn^{++} + \ominus \\ AgCl + \ominus = Ag + Cl^- \end{array}\right\} \quad (b)$$

$$\left.\begin{array}{l} \tfrac{1}{2}H_2O = H^+ + \tfrac{1}{4}O_2 + \ominus \\ Ag = Ag^+ + \ominus \end{array}\right\} \quad (c)$$

Thus oxidation (which occurs at the anode) consists in the loss of an electron, which is equivalent to an increase in the positive charge. For electrode reactions it is immaterial which custom is followed.

In all of these chemical reactions the anode reaction has been written first. A chemical reaction is merely a short way of writing the observed effects. Thus it will be noticed that the anode reactions for silver nitrate with a platinum anode and for copper sulfate with a platinum anode are the same. In each case oxygen is evolved and the hydrogen ion appears in solution at the expense of decomposed water. While it is sometimes stated that the sulfate ion discharges and then reacts with water to form sulfuric acid and oxygen, there is no experimental evidence for this statement. Even if this peculiar mechanism were true, it is a fact that no change in the number of sulfate ions finally results from the electrode reaction. The equations as written express the observed *facts*, and nothing is to be gained by combining these facts with fanciful assumptions such as the deposition of nitrate ions or of sulfate ions upon platinum.

Measurement of Quantity of Electricity.—The number of ampere-seconds or coulombs of electricity passing through an electric circuit is best measured through an application of Faraday's law, by weighing the metal deposited on an electrode placed in the circuit. Silver is deposited from silver nitrate solution upon a weighed platinum dish when accurate results are desired, and when the quantity of electricity involved is not too large.

The standard instruments in which this is done are shown[1] in Figs. 41 and 42. It is necessary that the increase in weight be due *only* to the

[1] *Bull. Bur. Standards*, **1**, 3 (1904).

electrolytic deposition of silver, and not to silver nitrate included in the crystals or to powdered silver from the disintegration of the anode, if accurate results are desired. To prevent inclusion of silver nitrate, the deposits are carefully washed with many portions of distilled water; it has been determined that inclusions of silver nitrate in a well-washed deposit[1] are not over 0.03 per cent, and they may be as low as 0.004 per cent.

Unless precautions are taken to prevent the electrolyte around the anode from reaching the cathode, deposits are obtained which are too heavy, due to the formation of some unknown substance at the anode (possibly colloidal charged silver) which deposits and is not removed by washing. Porous cups or perforated glass shields are placed around the

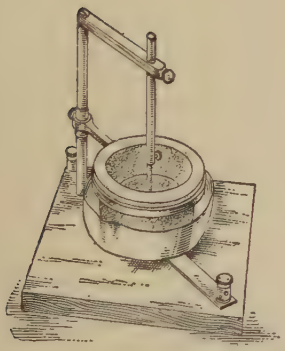


FIG. 41.—Porous-cup type of silver coulometer, set up for use.

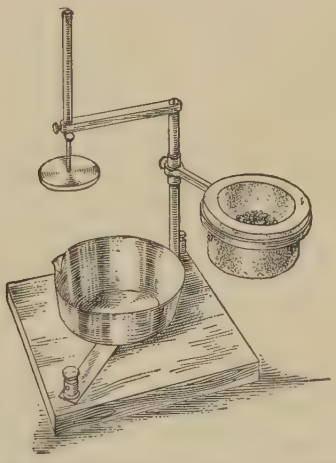


FIG. 42.—Parts of silver coulometer.

silver anode to avoid this disturbing factor. Exceptional care is used in securing pure silver nitrate for use in coulometers, as the presence of some other substance might lead to its inclusion in the weighed deposit. Such silver nitrate after very careful purification still gives high deposits if filter paper is wrapped around the dissolving silver anode. This simple means of protecting the cathode from dust falling off the anode during its electrochemical disintegration must therefore be condemned when careful work is being done. Presumably the soluble organic matter contained in even the best-washed filter paper exerts a reducing action upon silver nitrate, forming colloidal silver which is deposited on the cathode, or at least forming something which leads to a greater quantity of silver deposit per faraday than does pure silver in the absence of filter paper. Errors due to

[1] RICHARDS and ANDEREGG, *J. Am. Chem. Soc.*, **37**, 675 (1915).

filter-paper protection of anodes are usually less than a tenth of 1 per cent, and when this accuracy is sufficient, filter paper is not objectionable. But for the accurate work of which a silver coulometer is capable, filter paper must not be used. Porous clay pots are suitable vessels for protecting the cathode, and they are not of too high resistance for convenient use.

When commercial quantities of electricity are involved, the use of silver is out of the question, and copper is usually deposited from copper sulfate for this purpose. Lead from solutions of lead silicofluoride may also be used, or the volume of hydrogen evolved from a negative electrode in acid solution may be measured. The commercial processes of copper refining and electroplating of one metal upon another are everyday confirmations of the law of electrolysis. It is the universal experience in such processes that the weight of metal deposited is strictly proportional to the quantity of electricity passed through the electroplating cell when the current is not allowed to cause other reactions, such as the evolution of gas from the electrodes.

Resistance and Conductance.—The familiar law of Ohm that the current I, flowing in a conductor, is equal to E, the applied electromotive force divided by R, the resistance of the conductor, applies also to solutions which conduct electrolytically. This law, $I = E/R$, is often used in a form in which the resistance R is replaced by its reciprocal $1/R$, which is called the conductance, and denoted by L'. Ohm's law is then

$$I = EL'. \tag{1}$$

The specific resistance of a substance is the resistance of a centimeter cube of it, the reciprocal of this is the *specific conductance*, L. The conductance of any substance increases with its cross-section and decreases in proportion to its length. If the specific conductance is L, the conductance of a quantity of material in some other form than a centimeter cube is

$$L' = L\frac{q}{l}, \tag{2}$$

where q is the cross-section and l the length of the conductor. Conductance is expressed in reciprocal ohms; thus if the resistance is 175 ohms, the conductance is $1/175 = 0.005715$ reciprocal ohm.

Equivalent Conductance.—It is often more convenient to consider another property of a solution, called its equivalent conductance. Imagine two electrodes 1 cm. apart, parallel to each other, and of indefinite extent, between which is placed

such a quantity of solution that there is an equivalent of electrolyte present. Thus if the solution is normal, the volume of solution required is a liter, the cross-section of the conducting material is 1000 sq. cm.; if it is tenth normal, 10 liters of solution are required, and the cross-section of conducting material is 10,000 sq. cm. In the former case, this conductance is called the equivalent conductance of the normal solution, in the latter case the equivalent conductance at tenth normal, etc. In general, when there is an equivalent of electrolyte between two electrodes 1 cm. apart, the conductance is the *equivalent conductance* of the salt in question. The relation between equivalent conductance and specific conductance is shown by equation (2), where q is 1000 times the number of liters containing an equivalent, hence it is $1000/C$ if C represents the equivalent or normal concentration of the solution. In the example stated above, the equivalent conductance of a normal solution would then be $1000L$. If the solution is half normal, the volume containing it will be 2 liters, the cross-section 2000 sq. cm., and the equivalent conductance would be the new specific conductance $L_{0.5}$ multiplied by the new cross-section. This equivalent conductance is usually denoted by the Greek letter lambda with a subscript to indicate the concentration, thus $\Lambda_{0.5}$ for a half-normal solution. Then for any concentration the equivalent conductance is obtained by multiplying the specific conductance at that concentration by the cross-section of the conductor, which is the volume of solution containing an equivalent. The general relation is

$$\Lambda = \frac{1000L}{C} \text{ or } L = \frac{C\Lambda}{1000}. \qquad (3)$$

Equivalent Conductance and Concentration.—Suppose 10 c.c. of a normal solution of copper sulfate to be placed between two large copper plates 1 cm. apart, to which a potential of 1 volt is applied. As the conductance is numerically equal to the current flowing when the applied potential is unity, the current will be numerically equal to one-hundredth of the equivalent conductance, since one-hundredth of an equivalent is between the plates. If the temperature is 18°, $100I$, or the equivalent conductance of copper sulfate at normal, is 25.7. Now pour 40 c.c. of water between the plates, and stir. The quantity of copper sulfate between the plates is still 0.01 equivalent, but the con-

centration is 0.2 normal, and the equivalent conductance is now $100I = 37.7$; upon adding 50 c.c. of water, the concentration becomes 0.1 normal, and $100I = 43.8$. Correspondingly, if another 100 c.c. of water are added, the concentration is 0.05 normal, and $100I$ becomes 51.2; if 300 more are added, $100I$ is 62.4; if 500 more are added, so that the concentration is 0.01 normal, $100I = 71.7$. Further additions of water will cause a further increase in the current passing. The limit which the

TABLE 67.—EQUIVALENT CONDUCTANCES OF SALT SOLUTIONS

Normal Concentration	NaCl		KCl		HCl		$AgNO_3$	LiCl	NH_4OH	Acetic Acid
	18°	25°	18°	25°	18°	25°	18°	18°	18°	18°
0.0000	108.9	127.0	130.0	150.6	380.0	426.0	115.8	98.8	(239)	(350)
0.0001	108.0	.....	129.0	.....	378.1	.....	115.0	98.0	66	107
0.0005	107.1	.....	128.0	.....	377.0	.....	113.9	97.0	38	57
0.0010	106.4	124.1	127.3	.....	375.9	420.4	113.1	96.3	28	41
0.0020	105.5	123.1	126.2	146.6	375.3	418.6	112.1	95.4	20.60	30.20
0.0050	103.7	121.0	124.3	144.0	372.6	415.3	110.0	93.8	13.20	20
0.0100	101.9	118.7	122.4	141.4	369.3	411.6	107.8	92.0	9.60	14.30
0.0200	99.6	115.9	119.9	138.7	365.5	406.7	105.1	89.8	7.10	10.40
0.0500	95.7	111.2	115.7	133.7	358.4	398.4	99.5	86.0	4.60	6.48
0.1000	92.0	106.8	112.0	129.0	351.4	390.4	94.3	82.3	3.30	4.60
0.2000	87.7	101.7	107.9	124.2	342.0	380.2	.....	77.8	2.30	3.24
0.5000	80.9	93.5	102.4	118.8	327.	.....	77.5	70.6	1.35	2.01
1.0000	74.3	.....	98.2	117.4	301.	.....	67.6	63.3	0.89	1.32

Normal Concentration	HNO_3		KNO_3		$Ca(NO_3)_2$	CsCl	Na_2SO_4	$CaCl_2$	HF	$NaNO_3$
	18°	25°	18°	25°	18°	18°	18°	18°	18°	18°
0.0000	376.5	420.0	126.3	145.4	113.7	133.0	111.9	117.4	(361)	105.2
0.0001	.....	.....	125.4	.....	111.9	132.3	109.3	115.2	...	104.5
0.0005	373.9	417.0	124.3	.....	109.9	131.4	106.7	113.3	...	103.5
0.0010	372.9	.....	123.6	.....	108.5	130.7	105.1	112.0	...	102.8
0.0020	371.4	413.7	122.5	140.7	106.5	129.5	103.5	110.1	124	101.8
0.0050	371.0	.....	120.4	.....	103.1	127.5	99.8	106.7	77	99.97
0.0100	365.0	406.0	118.1	134.9	99.5	125.2	95.7	103.4	61	98.07
0.0200	364.0	.....	115.1	.....	95.2	.....	.....	99.4	48	95.57
0.0500	353.7	393.3	109.8	126.3	88.4	.....	83.6	93.3	36	91.35
0.1000	346.4	385.0	104.7	120.3	82.5	113.6	77.1	88.2	31	87.16
0.2000	340.0	.....	98.7	.....	76.0	.....	70.0	82.8	28	82.21
0.5000	324.0	.....	89.2	.....	65.7	.....	.....	74.9	27	73.99
1.0000	310.0	.....	80.4	.....	55.9	.....	.....	67.6	26	65.81

NOYES and FALK, *J. Am. Chem. Soc.*, **34**, 454 (1912).

conductance under these conditions approaches as the concentration approaches zero is called the equivalent conductance at zero concentration, or the limiting equivalent conductance. While the actual measurements are not carried out in this way, this will illustrate the meaning of equivalent conductance. The general trend for several substances is shown in Fig. 43, where the equivalent conductance is plotted against the logarithm of the concentration, to emphasize the slow increase at the lower concentrations.

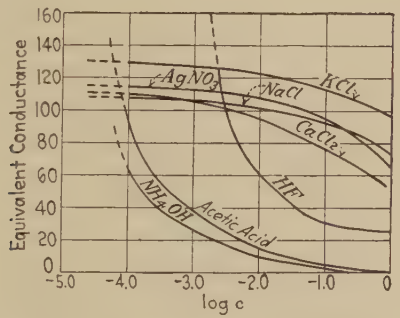


FIG. 43.—Change of equivalent conductance with concentration.

In Table 67 are given conductance data for several salts together with a limiting value obtained in a way explained below. These data will be needed in the solution of the problems at the end of the chapter.

Limiting Equivalent Conductance.—The limiting equivalent conductance which is approached as the concentration approaches zero, and which is supposed to correspond to "complete ionization," is not reached even at very low concentration, and it is difficult to make accurate measurements with extremely dilute solutions. However, this limiting value may be obtained by plotting the equivalent conductance against the concentration, extending or extrapolating the smooth curve thus formed to the axis corresponding to zero concentration, and reading off the value of the intercept. It is this value which is called the equivalent conductance at zero concentration, and which is written Λ_0. This is not the conductance of water; it is the limiting value which the equivalent conductance of the salt approaches

at very small concentrations. In these measurements, especially when the solutions are very dilute, the conductance due to water, or to impurities in it, is subtracted from the measured conductance before computing the equivalent conductance.

To decrease the uncertainty in extending the curve, it is common practice to plot some function of the conductance against the concentration, such that the resulting line is nearly straight. Thus Noyes and Falk[1]

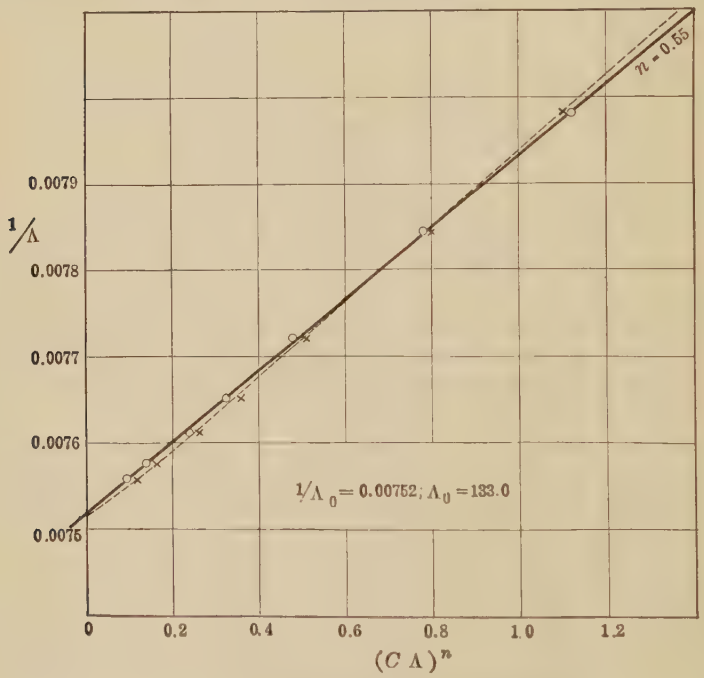


FIG. 44.—Extrapolation of conductance data.

plot the reciprocal of the equivalent conductance, $1/\Lambda$, against $(C\Lambda)^n$ and determine by trial the value of n (usually about 0.5) which gives a straight line through the points. Extension of this line to the axis corresponding to $(C\Lambda)^n = 0$ gives the limiting value of $1/\Lambda$, from which Λ_0 is readily obtained. Figure 44 shows how the data for cesium chloride (Table 67) at 18° are treated by this method, using 0.55 for the exponent. The dotted line of this figure was obtained by using $n = 0.50$, which gives a line somewhat more curved than $n = 0.55$

[1] *J. Am. Chem. Soc.*, **34**, 454 (1912).

Many other functions have been proposed for use in obtaining limiting values of the equivalent conductance, all of which depend upon plotting some conductance function against the concentration. The limiting conductances obtained by the various methods[1] agree to within about 1 per cent. For example, the limiting equivalent conductance of potassium chloride at 18° as estimated by any of the methods is between 129 and 130 reciprocal ohms, and the data of Table 68 show that this estimate is substantially correct. It will be observed that the equivalent conductance increases but little below 0.0001 normal.

TABLE 68.—CONDUCTANCE OF POTASSIUM CHLORIDE AT 18°

Equivalent concentration	Equivalent conductance	Ratio to limiting value
0.000	(129.64)	1.0000
0.00001	129.57	0.9995
0.00002	129.51	0.9990
0.00003	129.45	0.9985
0.00004	129.38	0.9980
0.00005	129.32	0.9975
0.00006	129.26	0.9970
0.00008	129.14	0.9961
0.00010	129.02	0.9953

WEILAND, *J. Am. Chem. Soc.*, **40**, 131 (1918).

It should be made clear that the limiting equivalent conductance is not the conductance of pure water, though it is often called the equivalent conductance at zero concentration, or at infinite dilution. In evaluating it the actual conductance of water is subtracted from the measured conductance. This value is the limit which the equivalent conductance approaches as the concentration is diminished and the cross-section of the conducting solution increases.

Measurement of Conductance.—In laboratory practice, the resistance of a solution is measured by means of a Wheatstone Bridge arrangement, using an alternating current of high frequency and a telephone receiver in place of a galvanometer. Such a resistance is chosen for the box that there is a point *b*

[1] RANDALL, *J. Am. Chem. Soc.*, **38**, 788 (1916); WASHBURN, *J. Am. Chem. Soc.*, **40**, 145 (1918); **42**, 1077 (1920); BATES, *J. Am. Chem. Soc.*, **35**, 519 (1913); KRAUS and BRAY, *J. Am. Chem. Soc.*, **35**, 1320 (1913).

(Fig. 45) near the middle of the bridge wire *abc* at which there is no sound audible in the telephone receiver. Then the resistance of the box is to that of the cell as the corresponding lengths of the uniform resistance wire *abc*; that is $R_{box} : R_{cell} = ab : bc$. The

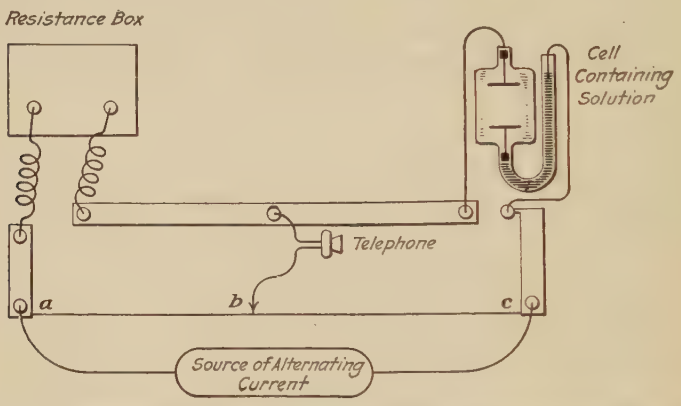


FIG. 45.—Arrangement of Wheatstone bridge for measuring conductivity of a solution.

reciprocal of this resistance is the conductance of the cell, and from its dimensions the specific conductance can be calculated by means of equation (2); then the equivalent conductance from equation (3).

The purpose of high-frequency alternating current is to avoid electrolysis of the solution during measurement. With frequent reversal of the current direction, any ion which might be deposited upon the electrode one moment would be dissolved from it the next moment.

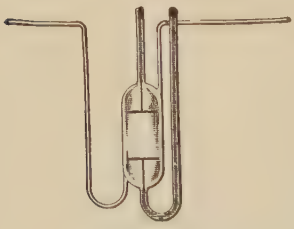


FIG. 46.—Conductance cell, pipet type.

A convenient form of cell in which to measure the resistances is shown[1] in Fig. 46. Contact with the electrodes is made through a glass seal into the tubes filled with mercury. Solution is drawn into the cell as into a pipet. As the electrodes are sealed up inside a glass vessel, they cannot be moved, and so alter the dimensions of that part of the solution between the electrodes. The electrodes are coated with platinum black to increase their surface, and eliminate polarization. Much work has been done recently in perfecting the apparatus for measuring conductivity, and each

[1] WASHBURN, *J. Am. Chem. Soc.*, **38**, 2449 (1916).

feature of the apparatus has been given careful study with a view to eliminating experimental errors. Clearly, nothing was to be expected in advancing the theory of electrolytes when there was uncertainty in the data. The best critical reviews are those of WASHBURN, *J. Am. Chem. Soc.*, **35,** 177 (1913); **38,** 2431 (1916); **40,** 106 (1918), and of ACREE, *Ibid.*, **38,** 2396 (1916). For a discussion of the preparation of water of sufficient purity see KENDALL, *J. Am. Chem. Soc.*, **38,** 2460 (1916); **39,** 9 (1917), and WEILAND, *J. Am. Chem. Soc.*, **40,** 131 (1918).

Conductance of Pure Water.—As stated above, the conductance of the water used in preparing a solution is subtracted from the measured conductance in determining that due to the salt. Careful experiments have shown that water is itself ionized to a slight extent, such that at 25° the concentration of hydrogen ion (and of hydroxide ion as well) is 0.0000001 normal. It is not from this source that most of the error in measuring conductivities of dilute solutions arises, but from the presence of dissolved impurities. Even after careful distillation, water may contain ammonia and carbon dioxide; and it will dissolve sodium and calcium salts from glass in a very short time. Perfectly pure water has a specific resistance of 25,000,000 ohms, ordinary distilled water a specific resistance of 100,000 ohms perhaps, and a good quality of "conductivity water" from 1,000,000 to 10,000,000 ohms. Water of a resistance greater than a million ohms per centimeter cube cannot be preserved in glass for more than a very few hours; perhaps for a day or so in quartz vessels. For this reason, conductivity water is freshly prepared for a set of measurements, first by distillation in the usual way, then by a second distillation (often directly into the conductivity apparatus) from alkaline permanganate solution, rejecting the first third of the distillate.

Change of Conductance with Temperature.—The equivalent conductance at any concentration changes rapidly with temperature, in the way shown in Table 69. For very dilute solutions the change is a linear increase of about 2 per cent per degree rise of temperature; but stronger solutions increase with temperature at a decreasing rate, as shown[1] in Fig. 47. For a solution which is half normal there is a point of maximum equivalent conductance at about 250°. Conductances of solutions above the boil-

[1] NOYES and COOLIDGE, *J. Am. Chem. Soc.*, **26,** 165 (1904).

ing point of water are made in a closed steel vessel capable of withstanding the pressure necessary to keep the solvent liquid.

TABLE 69.—CHANGE OF EQUIVALENT CONDUCTANCE WITH TEMPERATURE[1]

Salt	Equivalent concentration	Equivalent conductance at				
		18°	140°	218°	281°	306°
NaCl	0.0000	110.30	512	782	984	1078
	0.0005	107.18	493	747	926	1004
	0.0020	105.55	482	726	893	960
	0.0100	101.95	461	686	830	878
	0.1000	92.02	403	577	656	643
KCl	0.0000	131.40	572	845	1041	1125
	0.0005	128.11	...	...	.....	1051
	0.0020	126.31	538	786	950	1007
	0.0100	122.43	...	...	...	922
	0.1000	112.03	447	620	699	686

As the viscosity of water decreases rapidly with increasing temperature, the "fluidity" (reciprocal of the viscosity) increases.

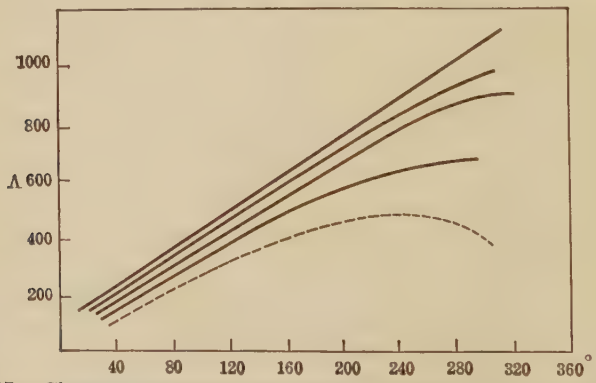


FIG. 47.—Change of equivalent conductance of sodium chloride with increasing temperature. The top line is Λ_0, the next lines are for 0.002, 0.01, and 0.1 normal; the dotted line is for half normal.

This rate of increase is about the same as the rate at which conductance increases. Recalling that conductance is the reciprocal

[1] NOYES and COOLIDGE, *J. Am. Chem. Soc.*, **26**, 134 (1904); JOHNSTON, *J. Am. Chem. Soc.*, **31**, 1010 (1909).

of resistance, it is seen that the decreased resistance of electrolytes nearly parallels the decrease in resistance to flow of the water. Hence it is very probable that the increase in equivalent conductance is largely due to the decrease in resistance to the motion of ions through water.

Transference Numbers.—The transference number of an ion in a solution may be defined as the fraction of the total electricity carried by that ion. It is obtained in the following way. The U-tube of Fig. 48 contains dilute hydrochloric acid, is fitted with a silver anode and a platinum cathode, and is surrounded by a constant-temperature bath and otherwise so treated that stirring of the solution is avoided, while 1 faraday of electricity passes through it. The solution is then withdrawn in three portions as shown by the dotted lines, and these are analyzed separately.

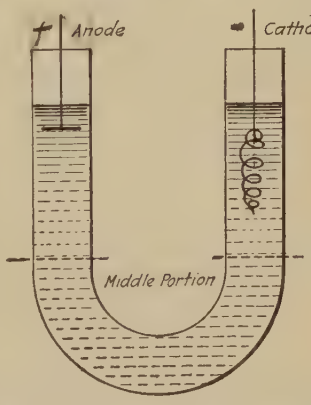


FIG. 48.—Diagram of transference apparatus.

It will be found that the concentration of the middle portion has not changed during the electrolysis, which shows that the quantity of hydrogen ion entering this portion from the anode region is equal to the quantity which has left the middle portion and entered the cathode portion; also the quantity of chloride ion entering the middle portion from the cathode region is equal to the quantity which has left the middle and entered the anode portion.

The *anode portion* has lost one equivalent of chloride ion during the electrolysis, according to the anode reaction

$$\mathrm{Ag(solid) + Cl^- + \oplus = AgCl(solid)},$$

where the symbol $\oplus$ indicates 1 faraday of positive electricity. But any portion of solution must at all times contain the same number of equivalents of positive ion as of negative ion; hence the loss of hydrogen ions into the middle portion plus the gain of chloride ions from the middle portion are together equal

to one equivalent, the loss of negative ions by electrolysis. That is, the anode portion has lost one equivalent of negative ion by electrolysis; it has gained part of an equivalent of chloride ion from the middle portion, and it has lost the remainder of an equivalent of positive ion to the middle portion. Equal quantities of positive and negative ions are, therefore, still present. Analysis shows that the quantity of hydrochloric acid in the anode portion has decreased 0.828 equivalent per faraday of electricity. But by electrolysis the anode portion lost one whole equivalent of chloride ion and no hydrogen ion. Then 0.172 (*i.e.*, 1 − 0.828) equivalent of chloride ion must have come into the anode portion from the middle portion and 0.828 equivalent of hydrogen ion must have gone out of the anode portion.

Let us now consider the *cathode portion*, where analysis shows that 0.172 equivalent of hydrochloric acid has been lost during the experiment. Hydrogen gas was evolved by the electrochemical reaction

$$H^+ = \tfrac{1}{2}H_2 + \oplus$$

and one equivalent of hydrogen ion was used up. But the loss in hydrogen ion as shown by analysis was only 0.172 equivalent; hence 1 − 0.172, or 0.828 equivalent of hydrogen ion, must have entered from the middle portion. This is just the quantity of hydrogen ion which entered the middle portion from the anode region; hence the middle portion has gained no hydrogen ion and lost none. Analysis shows the loss of 0.172 equivalent of chloride ion from this cathode portion, none of which entered into the electrolytic reaction. This, therefore, entered the middle portion, and it is equal to the quantity of chloride ion which was transferred into the anode portion from the middle portion. Upon comparing these figures with those obtained from the anode portion it will be seen that 0.828 equivalent of hydrogen ion has been transferred through the middle portion and 0.172 equivalent of chloride ion has been transferred through the middle portion in the opposite direction. Thus of the total electricity 0.172 was carried by chloride ion and 0.828 by hydrogen ion. These figures, being obtained from experiments in which the transfer of electrolyte from one portion of a solution to another is determined, are commonly called transference numbers of the ions.

The results obtained in this experiment may, for the sake of clearness, be summarized in "gain and loss tables" like the following:

Anode Portion			Cathode Portion	
Gain	Loss		Gain	Loss
	1.0 Cl^-	Electrolysis		1.0 H^+
0.172 Cl^-	0.828 H^+	Transference	0.828 H^+	0.172 Cl^-
	0.828 HCl	Net changes	0.172 HCl	

The transference number of an ion is the fraction of the total electricity carried by it through a solution. Table 70 shows

Table 70.—Transference Numbers of Positive Ions

Salt	Temperature	Concentration					
		0.005	0.01	0.02	0.05	0.10	0.20
NaCl	0°	0.387	0.387	0.387	0.386	0.385	
	18	0.396	0.396	0.396	0.395	0.393	0.390
	30	0.404	0.404	0.404	0.404	0.403	
KCl	0°	0.493	0.493	0.493	0.493	0.492	0.491
	18	0.496	0.496	0.496	0.496	0.495	0.494
	30	0.498	0.498	0.498	0.498	0.497	0.496
LiCl	18	.....	0.332	0.328	0.320	0.313	0 304
NH_4Cl	18	.....	0.492	0.492	0.492		
$AgNO_3$	18	.....	0.471	0.471	0.471	0.471	
	30	0.481	0.481	0.481	0.481	0.481	0.481
HCl	0°	0.847	0.846	0.844	0.839	0.834	
	18	0.832	0.833	0.833	0.834	0.835	0.837
HNO_3	20	0.839	0.840	0.841	0.844		
$BaCl_2$	0°	0.439	0.437	0.432			
	25	.....	.....	.....	0.438	0.427	0.415
$Ba(NO_3)_2$	25	.....	.....	.....	0.456	0.456	0.456
$MgSO_4$	18	0.388	0.385	0.381	0.373		
$CuSO_4$	18	.....	.....	0.375	0.375	0.373	0.361
K_2SO_4	18	.....	0.494	0.492	0.490		
	25	.....	.....	.....	0.496	0.494	0.493
H_2SO_4	20	.....	.....	0.822	0.822	0.822	0.820
Na_2SO_4	18	.....	0.392	0.390	0.383		
$CaCl_2$	20	0.440	0.432	0.424	0.413	0.404	0.395

Noyes and Falk, *J. Am. Chem. Soc.*, **33**, 1454 (1911).

such transference numbers for the positive ions in solution. It should be noted that the transference numbers change but little with the temperature. There is also a slight but significant change in transference number with the concentration. This matter will be referred to again in a later paragraph.

If the tube of Fig. 48 is filled with sodium chloride, sodium hydroxide forms at the cathode, and no sodium is lost from the tube; the reaction of chloride ion at the silver anode is the same as with hydrochloric acid. Analysis shows that the net loss of chloride ion from the anode portion of a solution of sodium chloride is 0.398 equivalent per faraday of electricity passed. Since a whole equivalent of chloride ion is lost by electrolysis, it follows that $1 - 0.398 = 0.602$ equivalent of chloride ion has entered the anode portion for each faraday of electricity passed. The quantity of electricity carried through the middle portion by chloride ions is, therefore, about 60 per cent of the total, and only 40 per cent has been carried by the positive ions. It should be remembered that the transference number of sodium ion in a solution of sodium chloride is not the same as in a solution of sodium nitrate or sodium acetate. This number is the fraction of the total electricity carried by the positive ion; whether the fraction carried by this ion is greater or less than half will depend upon the other ion of the electrolyte.

In calculating transference numbers from actual experimental data, there should be tabulated for each portion of solution, first, the change in each constituent due to electrolysis, then the net change found by analysis, and, finally, the change in each substance due to transference. These changes should be computed with reference to a fixed weight of water, not to a fixed volume or weight of solution; for in a solution the water alone remains stationary. A faraday is a very large quantity of electricity, and experiments are commonly carried out with a much smaller quantity. The total electricity passed through a solution is measured by a silver coulometer placed in series with the transference apparatus. Since the electrolysis and transference changes are both strictly proportional to the quantity of electricity passed, the values per faraday are calculated by simple proportion.

Limiting Conductances of the Separate Ions.—It has already been explained that each salt approaches a limiting equivalent

conductance as the concentration decreases. In very dilute solutions, where this limit is essentially reached, each ion is free to move about as if no other ions were present. From the transference number obtained in dilute solutions, and from the limiting equivalent conductance, may be calculated the limiting equivalent conductance of each ion in a solution. Thus the limiting equivalent conductance for sodium chloride at 18° is 108.9, and if this is multiplied by the transference number for sodium ion calculated above, 0.398, the result is 43.4 for the limiting conductance of the sodium ion, and 108.9 − 43.4, or 65.5, for chloride ion.

The limiting conductance for sodium nitrate is 105.2, 43.4 of which is due to sodium ion. Hence the equivalent conductance of nitrate ion is 105.2 − 43.4 = 61.8. For potassium nitrate the limiting value is 126.3; hence 126.3 − 61.8 = 64.5 is the equivalent conductance of potassium ion. The limiting value for potassium chloride should then be the sum of the values for potassium ion and chloride ion found above, or 64.5 + (108.9 − 43.4) = 130. Proceeding in this way, it is possible to calculate a value characteristic of each ion at each temperature. In Table 71 the limiting equivalent conductances of the separate ions at several temperatures are shown.[1]

Calculation of Conductance.—From such values the conductance of any solution involving ions may be calculated at any temperature by making a suitable estimate of the conductance ratio for the concentration in question. The conductance ratio Λ/Λ_0 is approximately the same for all salts of a given type at the same concentration, and this ratio changes only slightly with the temperature. For salts of different types the conductance ratio at a given concentration is not the same. Numerical values for the various types of salts may be found in Table 75, where they are marked C.R. When the equivalent conductance has been obtained for the concentration and temperature in question, the specific conductance follows from the relation $C\Lambda = 1000L$.

When such a calculation is desired at a temperature between those given, linear interpolation will give satisfactory results. For example, potassium nitrate in 0.1 normal solution has about

[1] JOHNSTON, *J. Am. Chem. Soc.*, **31**, 1010 (1909).

the same conductance ratio as potassium chloride, 0.86; the limiting conductances of its ions at 25° are 74.5 and 70.6. Then 86 per cent of the sum of these values, 124.8, is the equivalent conductance, and 0.01248 is the specific conductance. Its reciprocal is 81.0, the specific resistance of the solution; the measured specific resistance is 83 ohms. This represents about the average precision to be obtained in such calculations; often the agreement is much better, sometimes it is not so good. We have at least a useful method of calculating resistances where great accuracy is not desired.

TABLE 71.—LIMITING CONDUCTANCES OF IONS

Ion	Temperature							
	0	18	25	50	75	100	128	156
K^+	40.4	64.6	74.5	115	159	206	263	317
Na^+	26.0	43.5	50.9	82	116	155	203	249
NH_4^+	40.2	64.5	74.5	115	159	207	264	319
Ag^+	32.9	54.3	63.5	101	143	188	245	299
$\frac{1}{2}$ Ba^{++}	33	55	65	104	149	200	262	322
$\frac{1}{2}$ Ca^{++}	30	51	60	98	142	191	252	312
Cl^-	41.1	65.5	75.5	116	160	207	264	318
NO_3^-	40.4	61.7	70.6	104	140	178	222	263
$C_2H_3O_2^-$	20.3	34.6	40.8	67	96	130	171	211
$\frac{1}{2}$ SO_4^{--}	41	68	79	125	177	234	303	370
H^+	240	314	350	465	565	644	722	777
OH^-	105	172	192	284	360	439	525	592

The equivalent conductances for some other ions at 18° are Li^+ 33.3, $\frac{1}{2}Pb^{++}$ 60.8, $\frac{1}{2}Mg^{++}$ 46, $\frac{1}{2}Zn^{++}$ 47, Br^- 67.7, I^- 66.6, F^- 46.7, BrO_3^- 48.

Conductance of Mixtures.—The equivalent conductance of each salt in a mixture of salts with a common ion where the total concentration is $C_1 + C_2$ is roughly the same as that for each single salt *at the total concentration* $C_1 + C_2$. Thus, in a mixture which is 0.1 normal in sodium chloride and 0.5 normal in potassium chloride, the equivalent conductance for sodium chloride would be equal to its limiting conductance multiplied by the Λ/Λ_0 value for 0.6 normal sodium chloride, even though the sodium chloride itself is present only at 0.1 normal. In this way the equivalent conductance and then the specific conductance for

each salt should be calculated as if it were present alone. The specific conductance of the mixture is then the sum of the two separate specific conductances so calculated. The following example illustrates the method of calculation applied to a solution 0.05 normal in HCl and 0.10 normal in NaCl. When the total concentration is 0.15, Λ/Λ_0 is about 0.82 for salts of the KCl type. At 25° the limiting conductance of HCl is 424 and that of NaCl is 127. If the acid is 0.05 normal and the salt 0.10 normal, the respective specific conductances are

$$L_{HCl} = \frac{0.82 \times 424 \times 0.05}{1000} = 0.0174 \text{ and}$$

$$L_{NaCl} = \frac{0.82 \times 127 \times 0.10}{1000} = 0.0104.$$

The specific conductance of the mixture is the sum of these two quantities, or 0.0278; the measured specific conductance of this mixture is 0.0291. This illustrates about the degree of concordance to be expected from such a calculation.[1]

Limiting Velocities of the Separate Ions.—For an equivalent of electrolyte in dilute solution contained between parallel electrodes 1 cm. apart and of indefinite extent, the number of equivalents of each ion reaching an electrode per second will be the reciprocal of the velocity (in centimeters per second) of the ion toward the electrode under the applied potential. As the limiting equivalent conductance is approached, we may consider each constituent ion separately. In the ordinary expression for Ohm's law, $L' = I/E$, that part of the current due to a positive ion may be expressed as $N_c F/t$, where N_c is the number of equivalents of positive ion reaching the electrode, F is the value of Faraday's constant, and t is the time. If we consider the quantity of electricity passing in 1 sec., t becomes 1 and $N_c = 1/u_c$, where u_c is the velocity of the positive ion. It follows from the expression for Ohm's law that

$$u_c = \frac{\Lambda_c}{F E}.$$

When the applied potential is 1 volt for a column of solution 1

[1] A more accurate, but more complicated, method of calculating the conductance of mixtures which do not have an ion in common is given by SHERRILL, *J. Am. Chem. Soc.*, **32**, 741 (1910); see also BRAY and HUNT, *J. Am. Chem. Soc.*, **33**, 781 (1911) for measurements on mixtures of chlorides.

cm. long, the velocity of a sodium ion at 25° is 0.00053 cm. per second.

Hydration of Ions.—Mention has often been made of some peculiarity in the behavior of a solution as due to hydration, or a loose combination between solute and solvent. Thus the mol numbers of lithium chloride calculated from the osmotic pressure increased with increasing concentration, while mol numbers usually decrease with increasing concentration. Transference numbers are often found to change slightly with the concentration, probably on account of changing hydration. All of these effects are comparatively small, but they are not due to errors in the experimental data. In rough calculations these deviations are ignored, but much careful work has been done in seeking an explanation of them. No general explanation has been found, but hydration is certainly one of the factors responsible for some of the observed facts. We have no reliable method for determining the quantity of water combined with solute in a solution, though much work has been done in connection with freezing-point deviations,[1] and in other ways. There is, however, a method for determining whether the two ions of a solute carry different quantities of water or not, and this may be used to calculate the quantity of water combined with one ion if the other is *assumed* to carry none. Thus, suppose a transference experiment to be conducted upon a solution of sodium chloride to which has been added a little sugar. Sugar is not an ionized substance, it does not move through a solution when electricity is passed, and if at the end of an experiment the *ratio of sugar to water* in the electrode portions has changed, water must have come into this portion on the anion, or have been carried out of it on the cation.

When electricity passes through a normal solution of sodium chloride, 0.76 mol of water per faraday is lost from the anode por-

[1] Jones and others, *Carnegie Inst. Pub.*, **60** (1907). His data were calculated on the assumption that all deviations from the laws of ideal solutions were due to hydration of the solute, and led to the conclusion in some strong solutions (chromic acid, for example) that all of the water present was combined. This is, of course, absurd, for there could then be no solvent, but only solute. A review of hydration in general is given by Washburn, *Tech. Quart.*, **21,** 360 (1908), together with a criticism of each method.

tion, as shown by a change in the ratio of sugar to water. Assuming that the chloride ion does not carry any water, this 0.76 mol of water must have been carried out by 0.38 equivalent of sodium ion, this being the quantity of sodium ion leaving the anode portion per faraday passed. That is, each sodium ion is associated with two molecules of water, since 0.38 equivalent carried away 0.76 mol of water. There is, however, no ground for the assumption that chloride ions carry no water, but only the experimental fact that water has disappeared from the anode portion. Let us assume that a chloride ion carries four molecules of water. For each faraday of electricity passed, there is 0.62 equivalent of chloride ion entering the anode portion; this would bring in $0.62 \times 4 = 2.48$ mols of water. But there was a net loss of water, not a gain. Sodium ions have carried out 0.76 mol more water than chloride ions brought in, that is, $2.48 + 0.76 = 3.24$ mols, and this quantity of water moved on 0.38 equivalent of sodium ion. Hence $3.24/0.38 = 8.5$ mols of water per sodium ion, if the chloride ion carries 4 mols of water. This method gives only the difference in hydration; the actual hydrations calculated are based on some definite *assumption* as to the hydration of chloride ions, not on an experimentally established hydration of it. But as chloride ions cannot carry less than no water at all, two molecules of water on each sodium ion is the lower limit of its hydration. The mols of water moved per faraday of electricity are the result of experiment, based on the fact that sugar is not transported by an electric current; calculated values of hydration were made as explained above, and are shown in Table 72.

TABLE 72.—HYDRATION OF IONS[1] IN NORMAL SOLUTION

Salt	Mols water carried from anode to cathode per faraday of electricity	Transference number of positive ion	Mols water on positive ion when chloride ion is assumed to have		
			0	4	10
HCl	0.24	0.844	0.3	1.0	2.1
CsCl	0.33	0.491	0.7	4.7	11.0
KCl	0.60	0.495	1.3	5.4	11.5
NaCl	0.76	0.383	2.0	8.4	18.0
LiCl	1.50	0.304	4.7	14.0	28.0

[1] WASHBURN and MILLARD, *J. Am. Chem. Soc.*, **37**, 694 (1915).

The problem of solvation, in general, is still far from solved, though it is of the greatest importance in connection with the properties of solutions in general. There appears to be an intimate connection between the process of ionization itself and an affinity for water.[1]

Conductance in Solvents Other than Water.—Much scattered data exist on the ionization of substances in non-aqueous solvents,[2] but the conclusions stated in connection with experiments of various authors are often considerably at variance. Until more information is at hand, an attempt to treat the general subject of non-aqueous solutions very fully would be out of place.

A thorough study of ionization and electrical conductivity has been made upon anhydrous formic acid solutions;[3] and such solutions appear to be somewhat less complex in their behavior than water solutions. Thus the ion concentration calculated from the conductance ratio is identical with the effective concentration or activity, and the ions and non-ionized molecules exhibit approximately the behavior of ideal solutes. The fractional ionization decreases in strong solutions in a regular manner; limiting equivalent conductances are obtained in the same way as for water solutions; equivalent conductances are of the same order of magnitude as those in water. These data are given in Table 73.

Solutions of sodium iodide in acetone[4] and in isoamyl alcohol[5] also conduct electricity in much the same way as aqueous solutions; a limiting equivalent conductance is approached at small concentrations, and the ratio of this limiting value to the equivalent conductance at other concentrations is of the same

[1] KENDALL, *J. Am. Chem. Soc.*, **36,** 1069 (1914); DHAR, *Z. Elektrochem.*, **20,** 57 (1914); BOUSFIELD, *Trans. Faraday Soc.*, **15,** 73 (1919).

[2] The data on electrically conducting systems have been brought together in a single volume by C. A. KRAUS, "The Properties of Electrically Conducting Systems," Chemical Catalog Company (1922), to which reference may be made for detailed information concerning non-aqueous solvents.

[3] SCHLESINGER and his students, *J. Am. Chem. Soc.*, **41,** 1923 (1919).

[4] MCBAIN and COLEMAN, *Trans. Faraday Soc.*, **15,** 27 (1919).

[5] KEYES and WINNINGHOFF, *Proc. Nat. Acad. Sci.*, **2,** 342 (1916).

TABLE 73.—CONDUCTANCES IN ANHYDROUS FORMIC ACID AT 25°

Potassium Formate

Mols per liter of solution	Specific conductance	Equivalent conductance	Ratio to limiting value
0.000	.....	(68.92)	1.000
0.1027	0.006516	63.43	0.920
0.1314	0.008167	62.18	0.902
0.1992	0.01187	59.55	0.864
0.2433	0.01411	57.99	0.841
0.3104	0.01738	55.99	0.812
0.3266	0.01812	55.48	0.085

Sodium Formate

0.000	.....	(66.22)	
0.06418	0.003960	61.70	0.932
0.09682	0.005786	59.75	0.902
0.1755	0.009820	55.94	0.845
0.2337	0.01256	53.72	0.811
0.2734	0.01429	52.28	0.789
0.2954	0.01522	51.54	0.778
0.3153	0.01606	50.94	0.769

Lithium Formate

0.0000	.....	(64.72)	
0.0671	0.003917	58.38	0.902
0.1018	0.005689	55.86	0.863
0.1524	0.008061	52.90	0.817
0.2044	0.01030	50.38	0.778
0.2480	0.01203	48.51	0.750
0.3076	0.01423	46.24	0.714

order as that in water solutions. Table 74 shows the results of experiments.

TABLE 74.—CONDUCTANCE OF SODIUM IODIDE IN ACETONE AND ISOAMYL ALCOHOL

Equivalent concentration	Equivalent conductance in acetone			Equivalent conductance in isoamyl alcohol at 25°
	0°	25°	40°	
1.0000	.....	26.4	28.65	
0.5000	32.5	38.4	41.00	1.396
0.2000	44.9	52.7	56.60	1.339
0.1000	53.7	64.1	68.90	1.294
0.0500	63.1	76.1	82.70	
0.0200	77.2	95.0	103.80	1.649
0.0100	89.0	109.7	121.40	2.024
0.0050	99.0	124.5	139.40	2.560
0.0020	111.0	143.2	163.00	3.394
0.0010	118.5	155.0	178.00	4.184
0.0005	125.0	164.6	188.90	
0.0002	129.4	171.7	197.20	6.115
0.0001	129.9	173.6	199.90	6.636
0.0000	(131.4)	(176.2)	(204.00)	(7.790)

Conductance of Pure Liquids.—The conductance of water and of other pure liquids at ordinary temperatures is very slight, but it has been shown in the case of water to be due to a real ionization, and not to any impurities. The conductance of liquids increases with the temperature, quite rapidly in the case of water, but usually does not reach a point where the liquids are good conductors of electricity.

Fused salts are, on the other hand, very good conductors of electricity. The conductance is undoubtedly due to ions, just as that of their aqueous solutions is due to ions; the products of electrolysis are often the same as the products of electrolysis of their water solutions, except in cases where these would react with water. Fused lead chloride yields upon electrolysis lead at the cathode and chlorine at the anode; the same products result when aqueous solutions of it are electrolyzed.

Fused sodium hydroxide yields metallic sodium at the cathode and oxygen at the anode when it is electrolyzed; this same effect

is produced by electrolysis of sodium hydroxide solution with a mercury cathode in which sodium can dissolve and be protected from the action of water;[1] Faraday's law describes quantitatively the yield in both cases. But since salts in the fused condition are acting as both solvent and solute, ionic velocities have not yet been determined, and transference experiments are impossible, as appreciable concentration changes do not occur around the electrodes.

The industrial importance of electrolysis of fused salts is very great. Metallic sodium is produced almost entirely by electrolysis of fused sodium hydroxide; magnesium metal from the electrolysis of fused magnesium chloride; aluminum from the electrolysis of a solution of aluminum oxide in fused cryolite, a fluoride of sodium and aluminum. Some attempts have been made to develop the theory of fused salts,[2] but an adequate treatment of them has not yet been accomplished.

Ionic Theory

The *facts* regarding the behavior of ionized solutes have been given above. To account for these facts the ionic theory has been built upon the following assumptions about which there seems to be no serious doubt at the present time:

1. The molecules of certain substances spontaneously dissociate upon solution in water (and some other solvents) into two or more parts, bearing charges of electricity of opposite sign, and called ions.

2. The conduction of electricity by these solutions is due to the motion of ions through the solution. Positively charged ions move toward the negative pole; negatively charged particles

[1] When sodium hydroxide solution is electrolyzed with a platinum cathode, sodium does not deposit and then react with water to produce sodium hydroxide and hydrogen, as is sometimes stated. Hydrogen is evolved at the cathode and oxygen at the anode during this electrolysis, when the applied electrical potential is insufficient to cause the deposition of sodium. Metallic sodium is deposited in a mercury cathode as an amalgam only upon application of a much higher potential than is required to discharge hydrogen at a platinum electrode.

[2] See Kraus, "Electrically Conducting Systems," Chapter XIII for a discussion of these systems. The data referring to fused salts are collected in Vol. III of the International Critical Tables.

move toward the positive pole. Positive ions are called *cations*, since the electrode toward which they move is the *cathode*, and the reaction taking place there is the *cathode reaction*. Negative ions are *anions*, since the electrode toward which they move is the *anode*, and the reaction there produced is called the *anode reaction*.

3. Ions have charges which are exact whole multiples of a definite unit charge, that of the electron. Each negative ion in a chloride solution bears exactly the charge of an electron; nitrate ions, iodide ions, acetate ions, and all others which constitute a univalent group bear this same charge. Corresponding positive ions have charges of the same magnitude but opposite sign, and always in whole multiples of the unit charge; hydrogen, sodium, potassium, ammonium, and other groups bear a single positive charge, copper and magnesium a double charge, etc. This unit charge is 1.591×10^{-20} absolute electromagnetic units, or 1.591×10^{-19} coulombs; such a quantity of positive electricity is found upon each atom of sodium, and such a quantity of negative electricity upon each atom of chlorine in a solution of sodium chloride.

The original theory as formulated by Arrhenius and others also contains the following assumptions which are now being more or less seriously questioned:

4. The dissociation is not complete, but varies from a slight fraction in some cases (acetic acid and ammonium hydroxide) to a large fraction in other cases (salts, strong acids, and bases). In all solutions the fraction of dissolved substance dissociated into ions increases with decreasing concentration, and approaches unity (complete dissociation) as the concentration approaches zero.

5. Ions behave like *molecules of solute* as regards the properties of solutions which are determined by the mol fraction of the solute, such as vapor pressure, freezing point, boiling point, osmotic pressure. Each of these particles exerts the same effect upon the freezing point as a whole molecule. Non-ionized molecules exert their usual effects.

If all of these assumptions are granted for the moment, the experimental results given in the previous pages are subject to the following interpretation.

Degree of Ionization from Mol Numbers.—The mol numbers obtained from the freezing point or vapor pressure of solutions of the KCl type lead directly to a determination of the "fractional ionization," for if α is the fractional ionization and c the molal concentration of the salt, then each of the ions has the concentration $c\alpha$ and the undissociated salt has the concentration $c(1 - \alpha)$, giving a total of $c(1 + \alpha)$ mols of solute per formula weight. Some figures obtained by equating $1 + \alpha$ to the mol number are shown in Table 75.

Change of Equivalent Conductance.—It will be observed that all of the equivalent conductances given in Table 68 increase as the concentration decreases. This increase of equivalent conductance must involve some change in the condition of the ionized solute, for at each concentration there is one equivalent of solute between the electrodes. It has seemed reasonable to suppose that at lower concentrations a greater fraction of the solute became ionized; and that the limit which has been called "limiting equivalent conductance" corresponds to complete ionization of the solute. If it be assumed that the *only* change is in the fractional ionization, *i.e.*, that the ions have a fixed mobility, then the decrease in the equivalent conductance with increasing concentration is due to a decreased ion concentration, and the fraction ionized would be given by the ratio Λ/Λ_0. Now this assumption is certainly not correct, for it is shown in Table 70 that the transference numbers change slightly with the concentration. This means that one ion at least must be changing its mobility, and it is not certain that both ions may not change. Thus, if there is a decrease in the mobility of the ions at higher concentrations, this would give an apparent but not a real decrease in the "fractional ionization" if this is measured by the conductance ratio.

The "fractional ionization," as calculated from the conductance ratio, is marked "C.R." in Table 75 and is there compared with the "fractional ionization" calculated from mol numbers based on freezing point and marked "F.P." The agreement between the calculations based upon these two methods is rather close in many cases, but the differences are not due to errors in the experiments upon which they are based. Thus this comparison shows that at least one of these methods of calculating fractional ionization is incorrect.

TABLE 75.—COMPARISON OF PERCENTAGE IONIZATION[1] AS CALCULATED FROM FREEZING-POINT DEPRESSIONS (F.P.) AND FROM CONDUCTANCE RATIOS (C.R.)

		Equivalent concentration						
Salt	Method	0.005	0.01	0.02	0.05	0.10	0.20	0.50
KCl.....	F. P.	96.3	94.3	91.8	88.5	86.1	83.3	80.0
	C. R.	95.6	94.1	92.2	88.9	86.0	82.7	77.9
NaCl	F. P.	95.3	93.8	92.2	89.2	87.5	85.0	82.4
	C. R.	95.3	93.6	91.6	88.2	85.2	81.8	77.3
NH_4Cl	F. P.	94.7	92.8	90.7	87.8	85.6	83.2	
	C. R.	....	94.1	92.1				
$NaNO_3$.....	F. P.	....	90.3	88.5	85.5	83.0	79.8	
	C. R.	95.0	93.2	91.0	87.1	83.2	78.8	71.9
$KClO_3$.....	F. P.	....	91.4	89.1	84.9	79.8		
	C. R.	95.2	93.3	91.0	86.6	82.7	78.0	70.3
$BaCl_2$.....	F. P.	89.7	87.8	85.5	81.9	78.8	75.8	
	C. R.	....	88.3	85.0	79.8	75.9	72.0	67.2
$MgCl_2$.....	F. P.	....	....	88.5	85.4	83.9	83.3	
	C. R.	91.0	88.3	85.1	80.3	76.5	72.8	68.7
$Pb(NO_3)_2$....	F. P.	89.0	85.0	80.4	72.4	64.9	56.8	42.7
	C. R.	88.6	84.5	79.3	70.8	63.5	55.9	45.4
$MgSO_4$	F. P.	69.4	61.8	53.6	42.0	32.4	22.3	8.4
	C. R.	74.0	66.9	59.6	50.6	44.9	40.3	
$CuSO_4$.....	F. P.	61.6	54.5	45.5	31.8			
	C. R.	70.9	62.9	55.0	45.5	39.6	35.1	

Even if this difference is ignored, and the concentrations of ions and of non-ionized molecules are calculated from the "fractional ionization" based on either of the methods given, the change in ionization with changing concentration does not follow that to be expected from the law of mass action. Since

[1] NOYES and FALK, *J. Am. Chem. Soc.*, **34**, 485 (1912).

this law is so generally applicable to gaseous mixture and to solutions not containing ions, it is a matter of concern that it fails to apply to ions. We must, however, choose between two alternatives: (*a*) either the fractional ionization computed above is seriously in error, or (*b*) the laws of chemical equilibrium do not apply to ions. It has been pointed out[1] that the "degree of ionization" is a term which has never been precisely defined. The question might be put in the form "How far must the ions be separated in order to be completely dissociated?," for the ions in a molal solution of sodium chloride are "on the average" not over three times as far apart as in the solid crystal; and when a molal solution is diluted to 0.01 molal, the linear separation is increased by $\sqrt[3]{100}$, or about 4.5 fold.

Conductance and Ion Velocities.—Since the passage of positive electricity in one direction is, so far as an electric current is concerned, equivalent to the passage of an equal amount of negative electricity in the opposite direction, the total electricity carried through a cross-section of solution by its ions is equal to the sum of the equivalents of positive ion (cation) and of negative ion (anion) passing in their respective directions. That is, if N is the total number of faradays of electricity passing, and N_c and N_a are respectively the number of equivalents of positive and of negative ion crossing a given section,

$$N = N_c + N_a. \tag{4}$$

Let us consider first the positive electricity alone, that carried by positive ions in a solution containing C equivalents of ion[2] per liter, in a tube of cross-section q and length l, to which a potential of E volts is applied. When all of the positive ions have moved 1 cm., the quantity of positive electricity which has crossed a given line is equal to the charge upon all the positive ions in q c.c. of the solution, or $(C/1000)q$. The electricity passing per second on the positive ions is the product of this quantity and the distance moved by each positive ion per second, or

$$\text{Equivalents per second} = \frac{N_c}{t} = \frac{C}{1000}\,qV_c, \tag{5}$$

[1] Lewis, *J. Am. Chem. Soc.*, **43**, 1151 (1921).

[2] If fractional ionization is assumed to be measured by the conductance ratio, then this concentration will be Λ/Λ_0 times the equivalent concentration; and if complete ionization be assumed, this will be the concentration of the salt itself.

where V_c is the velocity of the positive ion. But $V_c = U_c E/l$, where U_c is the velocity under unit potential gradient, and E/l is the potential gradient. In t sec. the total quantity of positive ion crossing a given line is

$$N_c = \frac{C}{1000} qtU_c E/l. \tag{6}$$

A similar expression containing U_a, the velocity of the negative ion, shows the quantity of negative electricity passing, and the total quantity is given by

$$N = N_c + N_a = \frac{C}{1000} qt(U_c + U_a)\frac{E}{l}. \tag{7}$$

The current I is coulombs passing per second, and is by Ohm's law equal to E/R or to its equivalent EL'. If we denote by F the value of a faraday or 96,500 coulombs, the coulombs per second are NF/t. The current flowing is obtained by multiplying both sides of equation (7) by F/t.

$$I = \frac{NF}{t} = \frac{C}{1000} Fq(U_c + U_a)\frac{E}{l} \tag{8}$$

The specific conductance is equal to $L'l/q$, or since $I = EL'$, it follows from equation (8) that

$$L = \frac{C}{1000}(U_c + U_a)F. \tag{9}$$

Upon substituting in this equation the relation $1000\ L = C\Lambda$, from equation (3), we obtain

$$(U_c + U_a)F = \Lambda, \tag{10}$$

from which it is possible to calculate roughly the mobilities of the ions when we know the fraction of the equivalent conductance due to each ion. For instance, in potassium chloride the transference numbers are each about 0.50. Assuming them equal, we may calculate the limiting velocity U from the limiting equivalent conductance, $\Lambda_0 = 130$, since $2UF = 130$, and it follows that $U = 130/(2 \times 96{,}500) = 0.000674$ cm. per second. This will give an idea of the velocity of an ion toward an electrode when the potential applied is 1 volt for each centimeter between electrodes.

Assumption of Complete Ionization

In many journal articles which are appearing on the theory of ionized solutes, the statement appears that complete ionization is assumed.[1] This should not be understood to mean that hydrogen chloride gives 2 mols of ideal solute per formula weight, but only that for the time being the properties of these solutions will be considered in the light of other functions than a supposed fractional ionization. The experimental basis for this assumption seems to be that certain properties of the solutions are additively properties of the ions. Until it has been shown that these properties would change significantly with the extent of ionization, this evidence hardly proves more than would additivity in mass. The assumption is not to be applied, except to dilute solutions of "largely" ionized solutes. For example, there is strong evidence that acetic acid in a molal solution is less than 1 per cent ionized and it would be absurd to apply an assumption of complete ionization to it.

The fact that the law of mass action is consistent with the change in "fractional ionization" (as measured by the conductance ratio) for changing concentrations of slightly ionized solutes in water, and for many solutes in other solvents such as liquid ammonia, makes it improbable that complete ionization is a general phenomenon. Thus if Λ/Λ_0 is the "fractional ionization" and C is the molal concentration of acetic acid, $C\Lambda/\Lambda_0$ is the concentration of hydrogen ion or of acetate ion and $C(1 - \Lambda/\Lambda_0)$ is the concentration of non-ionized acetic acid. The law of mass action requires that

$$\frac{[C\Lambda/\Lambda_0]^2}{C(1 - \Lambda/\Lambda_0)} = \text{const.}$$

This will be taken up again in Chapter VIII. Even if it should prove true that salts in dilute aqueous solutions are completely ionized, this should probably be considered as a special case in a general theory of ionization.

[1] Noyes and MacInnes, *J. Am. Chem. Soc.*, **42**, 239 (1920); Sutherland, *Phil. Mag.*, **3**, 161 (1902); **12**, 1 (1906); **14**, 3 (1907); Milner, *Phil. Mag.*, **35**, 214, 354 (1918); *Trans. Faraday Soc.*, **15**, 148 (1919); Ghosh, *J. Chem. Soc. London*, **113**, 449 (1918); *Trans. Faraday Soc.*, **15**, 154 (1919); Bjerrum, *Z. Elektrochem.*, **24**, 321 (1918); Kraus, "Electrically Conducting Systems," p. 349.

The Activity Function.—The activity of any constituent of a system has been defined by Lewis[1] as its mass-action affect. For any ion solute the activity would then be the mass-action effect which it produces in solution. Following the notation of Lewis and Randall,[2] the activity of a solvent is designated by a_1 and of a solute by a_2. Thus the vapor pressure of solvent over a solution would be proportional to a_1, and for an ideal solvent this could be computed from Raoult's law. No simple law for calculating the activity of an ionized solute has yet been discovered. We may, however, designate by a_+ and a_- the activities of the positive and negative ions respectively, and by a_2 the activity of the non-ionized molecules. Then by definition

$$\frac{a_+ a_-}{a_2} = K.$$

In the complete absence of any information regarding the concentration of non-ionized solute in an electrolytic solution, Lewis further defines K as unity so that

$$a_+ a_- = a_2.$$

Since at finite concentrations the two ions of a solute may not have the same activity, it is often expedient to consider the geometric mean of the two ion activities, which may be defined

$$a_\pm = \sqrt{a_+ a_-}.$$

The Activity Coefficient.—Lewis further defines the activity coefficient as the activity divided by the molality, that is,

$$\gamma = \frac{a_\pm}{m}.$$

It will be seen that this function is similar to a degree of dissociation and it is sometimes called the thermodynamic or "corrected" degree of dissociation. It is, however, much better to call it the *activity coefficient*, since in concentrated solutions its value may be greater than unity. As γ cannot be calculated for one salt when it is known for another one, or even for the same salt at a different concentration, except from empirical equations based on data for activity itself, this is substantially an

[1] *Proc. Am. Acad. Arts Sci.*, **43**, 259 (1907).

[2] *J. Am. Chem. Soc.*, **43**, 1112 (1921).

empirical treatment of ionized solutes. We shall confine our discussion to the simplest type of solute, that is, to one of KCl type. The equations for more complex types, such as $BaCl_2$ and for the $CuSO_4$ type, are given by Lewis and Randall in the reference quoted above.

Methods of Determining an Activity Coefficient.—The activity coefficients may be obtained from vapor-pressure determinations when the ionized solute is sufficiently volatile, since the

TABLE 76.—MEAN ACTIVITY COEFFICIENTS OF THE IONS OF POTASSIUM CHLORIDE AT 25°

Molality	Lewis and Randall[1] freezing points	Noyes and MacInnes[2] e.m.f.	Lewis and Randall[1] e.m.f.	Scatchard[3] freezing points	Scatchard[3] e.m.f.
0.001	0.977	0.979	0.984	0.966	0.965
0.002	0.967	.....	0.971	0.952	0.951
0.005	0.946	0.923	0.947	0.928	0.926
0.01	0.922	0.890	0.924	0.902	0.899
0.02	0.892	.....	0.894	0.870	0.865
0.05	0.841	0.790	0.860	0.818	0.809
0.1	0.796	0.745	0.814	0.772	0.762
0.2	0.749	0.700	0.783	0.719	0.715
0.3	.....	0.673	0.768	0.686	0.688
0.4	.....	.....	0.763	.....	0.669
0.5	0.682	0.638	0.762	.....	0.654
0.6	.....	.....	0.770	.....	0.642
0.75	.....	.....	0.788	.....	0.627
1.0	0.634	0.593	0.823	.....	0.605

activity is proportional to the vapor pressure.[4] The activity of the solute may be calculated from the vapor pressure of the solvent by means of a thermodynamic equation,[5]

$$d \ln a_1 = -\frac{N_2}{N_1} d \ln a_2,$$

[1] *J. Am. Chem. Soc.*, **43**, 1112 (1921).
[2] *J. Am. Chem. Soc.*, **42**, 239 (1920).
[3] *J. Am. Chem. Soc.*, **47**, 654 (1925).
[4] BATES and KIRSCHMANN, *J. Amer. Chem. Soc.*, **41**, 1991 (1919).
[5] See LEWIS and RANDALL'S "Thermodynamics" for methods of using this equation.

in which N_1 and N_2 are the mols of solvent and solute, and a_1 and a_2 are the corresponding activities. The activity coefficients are usually calculated from the electromotive force of a series of cells involving the same electrodes and solutions of the solute at different concentrations in a manner to be described in Chapter XVI. They may also be calculated from freezing-point determinations, provided these cover a range of concentrations extending at least as low as 0.001 molal, but the method of calculation is too complex for beginners.[1] The figures in Table 76 give the results of the several methods for the mean activity coefficient for potassium chloride, as applied by various investigators. From the marked divergence among the coefficients calculated for higher concentrations it is evident that much still remains to be done in this field of endeavor.

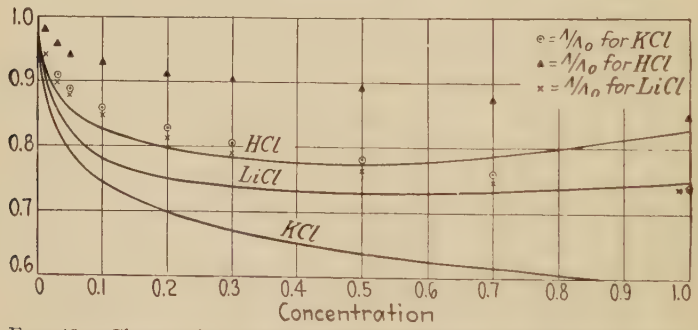


FIG. 49.—Change of Λ/Λ_0 and of activity coefficient with concentration.

Since the activity coefficient is defined in such a way that it becomes unity as the concentration approaches zero, the methods of calculating the activity coefficients depend upon extrapolating some function of the activity to zero concentration. The divergence among the activity coefficients for potassium chloride, shown in Table 76, is largely due to the extrapolation of different functions. In Fig. 49, the lines show the change of activity coefficient with the concentration and the dots of characteristic shape illustrate the divergence between this activity coefficient and the conductance ratio.

Activity Coefficients of Simple Electrolytes.—We give here for future reference a table of activity coefficients for alkali chlorides.

[1] See LEWIS and RANDALL'S "Thermodynamics" for methods of using this equation.

TABLE 77.—MEAN ACTIVITY COEFFICIENTS OF THE IONS AT 25°[1]

Molality	KCl	NaCl	LiCl	HCl	KOH
0.001	0.965	0.966	0.965	0.966	0.965
0.002	0.951	0.953	0.952	0.954	0.952
0.005	0.926	0.928	0.927	0.932	0.927
0.01	0.899	0.903	0.901	0.910	0.901
0.02	0.865	0.871	0.869	0.881	0.868
0.05	0.809	0.821	0.819	0.836	0.815
0.1	0.762	0.778	0.779	0.801	0.772
0.2	0.715	0.734	0.750	0.774	0.739
0.3	0.688	.....	0.739	0.763	0.727
0.4	0.669	.....	0.735	0.760	0.723
0.5	0.654	0.671	0.736	0.763	0.723
0.6	0.642	.....	0.738	0.770	0.725
0.75	0.627	.....	0.743	0.783	0.731
1.0	0.605	0.634	0.753	0.817	0.743

The mean activity coefficient for simple electrolytes in a mixture[2] of two salts at a total concentration of $c_1 + c_2$ is about the same as that for each salt when it is alone present at the concentration $c_1 + c_2$. Accurate data on the activity coefficients in mixtures have shown that this simple rule is not strictly true,[3] but so far no accurate general law has been discovered.

Interionic Attraction Theory.—A theory has recently been proposed which is commonly known as the Debye and Hückel[4] theory. The fundamental idea underlying it is that, owing to electrical attraction between positive and negative ions, there are, on the average, in the neighborhood of any ion more ions of unlike sign than of like sign. Consequently, when such a solution is diluted the separation of the ions involves performing internal work against this electrical attraction, and a corresponding increase in the energy content of the solution. Upon this

[1] SCATCHARD, *J. Am. Chem. Soc.*, **47**, 660 (1925).

[2] A rule for mixtures which is more exact than this is given by LEWIS and RANDALL, *J. Am. Chem. Soc.*, **43**, 1112 (1921), in terms of the ionic strength, which is half the sum of the molality of *each ion* multiplied by the square of its valence. For example, in 0.01 molal KCl the ionic strength is 0.01, but in 0.01 molal $BaCl_2$ it is $(0.01 \times 2^2 + 0.02)/2 = 0.03$.

[3] See, for example, papers by HARNED, *J. Am. Chem. Soc.*, **47**, 676 (1925).

[4] *Physik. Z.*, **24**, 185 (1923); HÜCKEL, **26**, 93 (1925). This theory has been reviewed by A. A. NOYES in *J. Am. Chem. Soc.*, **46**, 1080 (1924).

assumption, together with the assumptions (*a*) that ionization is complete; (*b*) that the volume of the ions is negligible in comparison to the space between them; and (*c*) that the dielectric constant of the medium does not change with the temperature, the following expression has been derived to show how the logarithm of the activity coefficient changes with the concentration in a "dilute" solution:

$$ln\ \gamma = e^3N^2\sqrt{\frac{\pi}{R}}\left(-\frac{\nu^2\sqrt{\Sigma c\nu^2}}{R(KT)^{1.5}}\right).$$

In this expression ν is the valence of the ion, R is the gas constant, K is the dielectric constant of the solvent, T is the absolute temperature, e is the electronic charge, c is the ion concentration per cubic centimeter, and N is Avogadro's number. For an aqueous solution of a salt of the KCl type at 25° this equation may be reduced to the following one in which all of the constants are combined into a single term:

$$-\log\gamma = 0.357\sqrt{2c},$$

where c is now the molality of the solution. It will be noted that this equation contains no term which is characteristic of the solute.

A similar equation has been developed by Milner[1] which for dilute solutions reduces to the same form with a different numerical constant. Activity coefficients calculated from the Debye-Hückel equation (theory *a*) and the Milner equation (*b*) are compared with measured values in Table 78. An examination of these figures shows at once that the equation, as simplified for "dilute" solutions, is incorrect, or that solutions of this concentration are not sufficiently "dilute." A form of the equation which takes into account the "size of the ions" and the variation in dielectric constant of the solvent with the salt concentration has been given[2] which brings the calculated and measured activity coefficients into much better agreement. The mathematical derivation by Hückel is very complex, and as yet the numerical factors in this modified equation may not be calculated except

[1] *Phil. Mag.*, **23,** 551 (1912); **25,** 742 (1913).

[2] Hückel, *Physik. Z.*, **26,** 93 (1925); see also Brönsted and La Mer, *J. Am. Chem. Soc.*, **46,** 555 (1924); Scatchard, *J. Am. Chem. Soc.* **47,** 648, 2098 (1925); Noyes and Baxter, *J. Am. Chem. Soc.* **47,** 2122 (1925).

from measurements leading to the activity coefficient itself, so that the equation becomes an empirical one. Research and study upon this equation have only just begun, and a critical discussion of it would be premature. The final equation of Hückel for the case of a salt of the KCl type is

$$\log \gamma = -\frac{0.354\sqrt{2c}}{1 + 0.23 \times 10^8 a\sqrt{2c}} + B2c,$$

where a is the "diameter of the ions" and B is a constant. It is significant that the value of a which satisfies the requirement of this equation is 2.35×10^{-8} for sodium chloride, which is of the same order of magnitude as atomic diameters found in other ways. The spacing of 100 planes in sodium chloride is 2.81×10^{-8} cm.

TABLE 78.—EXPERIMENTAL AND THEORETICAL VALUES OF THE ACTIVITY COEFFICIENT PRODUCT COMPARED

Substance	Formula weights per 1000 grams of water				
	0.01	0.02	0.05	0.10	0.20
Theory (*a*)	0.792	0.720	0.594	0.480	0.354
Theory (*b*)	0.823	0.761	0.650	0.542	0.421
HCl	0.854	0.801	0.740	0.662	0.612
LiCl	0.852	0.799	0.711	0.647	0.600
NaCl	0.852	0.799	0.710	0.639	0.568
KCl	0.852	0.799	0.706	0.630	0.561
KOH	0.852	0.799	0.706	0.629	

This table is taken from page 1101 of the article by Noyes, quoted above. The activity coefficients marked (*a*) result from the equation $\log \gamma = -0.357\sqrt{2c}$ and those marked (*b*) from $\log \gamma = -0.298\sqrt{2c}$.

Procedure to Be Followed in This Book.—From the discussion in this chapter it will be seen that the conductance ratio does not measure the "activity coefficient" by which the salt concentration must be multiplied in order to give the mass-action effect of an ion. In the present state of our knowledge the calculation of an activity coefficient is difficult and somewhat uncertain, even in a moderately concentrated solution containing one salt

of the simplest type. Comparatively little work has been done upon the activity coefficients for ions in mixtures of salts. In the treatment of chemical equilibrium in the following chapters it would be very desirable to multiply the concentration of each salt by the appropriate activity coefficient if this were known. It is, however, unknown and we shall therefore make the calculations by using the salt concentration itself without an activity coefficient as a rough measure of the activity. In so doing we do not assume complete ionization or incomplete ionization; and we shall use the salt concentration in place of activity with the full understanding that this procedure is not correct. In many calculations, however, the activity coefficient, if inserted, would cancel out.

Until such time as the theory of ionized solutes is upon a more secure basis than at present, it does not seem best to try to take activity coefficients into account. When there is reason to believe that the solute is substantially un-ionized we shall treat it as if it were not ionized. Cases involving solutes which are not "largely ionized" but which are not substantially un-ionized will not be treated at all in this text.

Questions

Numerical data for solving these problems should be sought in the tables.

1. What weight of copper would be deposited by a current of 10 amperes flowing through copper sulfate solution for 24 hr.? How long would it take to deposit a ton of copper if a current of 2000 amperes was used? A ton is 906 kilos.

2. It is desired to plate a square foot of sheet iron with a layer of copper 0.1 mm. thick in 12 hr. What current will be required? The density of copper is 8.95; both sides of the sheet are to be covered.

3. How long would a current of 1 ampere flow in order to liberate a gram of iodine, atomic weight 126.9? What weight of silver (atomic weight 107.88) would be deposited by the same quantity of electricity?

4. Calculate the values of $1/\Lambda$ and of $(C\Lambda)^{\frac{1}{2}}$ for each concentration of silver nitrate given in Table 67. Make a plot of these values, and by drawing the best straight line through the points determine the value of the intercept of the line on the axis $C\Lambda = 0$. From this intercept, calculate a value for the limiting equivalent conductance of silver nitrate.

5. Plot the values of the equivalent conductance of sodium formate in anhydrous formic acid against the concentration, draw a smooth curve through the points and extend this curve to the axis corresponding to zero concentration to determine the limiting equivalent conductance.

6. A dilute solution of nitric acid is electrolyzed between platinum electrodes. Predict the net changes, expressed in equivalents of acid, resulting in each electrode portion per faraday of electricity passed through the solution. Hydrogen ion moves five times as fast as nitrate ion, and the anode process consists in the evolution of oxygen gas.

7. A transference tube is filled with 0.1 formal $LiNO_3$ and fitted with a silver anode. The anode portion before electrolysis contained 10.00 grams $LiNO_3$, and after electrolysis 1.00 grams of $AgNO_3$ and 9.858 of $LiNO_3$. Calculate for each ion the equivalents gained or lost in the anode portion. What is transference number of Li^+ in $LiNO_3$?

8. A solution 0.1 normal in sodium sulfate is electrolyzed in a transference apparatus with a platinum anode and a AgCl cathode. After electrolysis 83 c.c. of 0.2 normal alkali are required to neutralize the acid formed in the anode portion, and the cathode portion has lost 0.0100 equivalent of sulfate. (*a*) What is the transference number of sulfate ion? (*b*) How many equivalents of NaCl are in the cathode portion? (*c*) How much sodium has been lost from the anode portion by transference?

9. The transference number of hydrogen ion in H_2SO_4 is 0.82. Calculate changes in equivalents of each constituent in the anode portion and in the cathode portion from electrolysis and from transference if a current of 1 ampere is passed for 1 hr. through H_2SO_4 between a lead anode and a cathode of PbO_2. Assume that only H^+ and SO_4^- ions are present.

10. A tenth formal solution of lithium iodide is electrolyzed in a transference experiment. The electrodes consist of a platinum anode and a silver iodide cathode. By titration with thiosulfate solution, it was found that the anode portion contained 1.27 grams of free iodine. The net gain of lithium iodide in the cathode portion is 0.445 gram. (*a*) Construct a "gain and loss" table for both anode and cathode portions. (*b*) Calculate the transference number of the iodide ion.

11. A solution containing 6.00 grams of $MgSO_4$ per 1000 grams of water is electrolyzed between platinum electrodes. The anode portion weighs 80.59 grams, and requires 45 c.c. of 0.1 normal NaOH to neutralize the sulfuric acid formed. It yields on analysis 0.366 gram of $MgSO_4$. (*a*) Calculate the weights of $MgSO_4$, H_2SO_4, and water contained in it. (*b*) Write a complete gain and loss table *per faraday* for the anode portion. (*c*) Calculate the transference number of magnesium ion.

12. A transference experiment is made with a solution containing 7.39 grams of silver nitrate per 1000 grams of water, using two silver electrodes. A silver coulometer in the circuit shows a deposit of 0.0780 gram of silver. At the end of the experiment the anode portion weighing 23.38 grams is found on analysis to contain 0.2361 grams of silver nitrate. (*a*) Calculate the transference numbers of the silver and nitrate ions. (*b*) The cathode portion weighs 25.00 grams. How much silver nitrate does it contain?

13. In a transference experiment 0.01 faraday was passed at 25° through a solution placed between copper electrodes and containing 15 96 grams of $CuSO_4$ and 17.00 grams of NH_3 in 1000 grams of water. The anode portion withdrawn at the end of the experiment weighed 103.7 grams and contained

2.091 grams of $CuSO_4$, and 1.571 grams of NH_3. Determine from these data the formula for the copper-ammonia complex, and the transference number of the $Cu(NH_3)_x$ ion. Assume that all of the copper in the solution is combined with ammonia.

14. A 0.1 formal hydroiodic acid solution is electrolyzed in a transference apparatus with silver-silver iodide electrodes. An anode portion weighing 250 grams is found to be 0.0641 formal in hydroiodic acid. The weight of silver deposited in a silver coulometer in series was 1.078 grams. (*a*) Write the electrode reactions. (*b*) Construct gain and loss tables for the anode and cathode portions. (*c*) Calculate the transference number of the hydrogen ion.

15. A current of 50 milliamperes is passed for 5 hr. through a dilute solution of sodium bromide between silver electrodes coated with silver bromide. Describe quantitatively the changes that occur in each electrode portion in accordance with Faraday's law and with the law of transference. Make also a quantitative statement of the net effect of these changes in each portion. Silver bromide forms at the anode, silver bromide is reduced to metallic silver at the cathode, and the transference number of bromide ions is 0.61.

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16. State briefly the fundamental assumptions of the ionic theory. What facts have supported each of them?

17. Summarize the facts which have led to the hypothesis that salts are completely ionized in solution.

18. A solution 0.1 formal in nitric acid freezes at $-0.35°$. Calculate the fraction of it which is ionized. From this result, and the limiting conductances of its ions, calculate the specific resistance of the solution at 25°.

19. Calculate the specific resistance at 0°C. of a 1 per cent solution of sodium chloride. Calculate the same resistance at 100°.

20. In a rectangular trough 20 cm. long, provided with a copper electrode at each end, are poured 100 c.c. of 0.1 normal $CuSO_4$ solution. With 100 volts at the electrodes what is the resultant current?

21. A sample of "hard water" known to contain only calcium sulfate and calcium bicarbonate in appreciable quantities is submitted for analysis. At 18° the specific conductance of the hard water is 0.00100. It is boiled (without loss of water) and cooled to 18°, when its specific conductance is found to be 0.000757. Assuming that each salt is 85 per cent ionized and that boiling completely changes the calcium bicarbonate to insoluble $CaCO_3$, calculate the concentration of calcium sulfate ("permanent hardness") and of calcium bicarbonate ("temporary hardness"), expressing the results as formula weights per liter. The equivalent conductances are Ca = 52, SO_4 = 68.5, HCO_3 = about 35.

22. A 0.1 normal solution of NaCl has at 18° a specific resistance of 108.7 ohms. In a given transference experiment this solution is electrolyzed between a silver anode and a silver cathode coated with silver chloride; the anode is found to gain in weight by 0.177 gram, and the cathode portion to increase its content in sodium chloride by 0.117 gram. (*a*) Calculate the equivalent conductance of the sodium ion at 18°. (*b*) Calculate the rate,

expressed in centimeters per hour, at which the chloride ion would migrate through the solution at 18° under a potential gradient of 2 volts per centimeter.

23. (*a*) Calculate the specific conductance at 18° of 0.05 formal $BaCl_2$, assuming it is 12 per cent ionized into $BaCl^+$ and Cl^-, and 65 per cent ionized into Ba^{++} and Cl^-. (*b*) Calculate the freezing point of the solution. Assume the equivalent conductance of the intermediate ion $BaCl^+$ to be 25.

CHAPTER VII

THERMOCHEMISTRY

The heat effects of chemical changes have attracted the attention of chemists almost from the beginning of exact work in chemistry. It was thought for a long time that the heat evolved during a chemical reaction was a measure of the "chemical affinity" of the substances combining, since those reactions which proceed with the evolution of large quantities of heat (such as the combustion of carbon or of hydrogen) result in the formation of very stable molecules. That the "chemical affinity," or driving force of a reaction, could not be measured in this way was realized after the discovery of reactions which proceeded of themselves, but with the *absorption* of heat from the surroundings. The problems of thermochemistry did not become on that account less interesting or of less importance; indeed, they led the way to the discovery of the true relation between chemical driving force and reaction heat. Heats of reaction are of great importance in calculating chemical equilibrium at one temperature from the experimental data at another temperature, and in many other ways which will appear later in their proper places.

Thermochemical Methods.—A reaction whose heat effect is desired is carried out in a suitable vessel immersed in a tank of water, which must be protected from losses of heat to its surroundings. The rise in temperature of this tank (called the calorimeter) is determined by a sensitive thermometer or by other means, and from this rise and the known heat capacity of the calorimeter is calculated the heat effect. In order to prevent any loss of heat by exchange between the calorimeter and its surroundings, these are often maintained at the same temperature as the calorimeter itself. As the temperature of the calorimeter rises during a reaction produced in it, a parallel rise is produced in the surroundings, usually by adding sulfuric acid

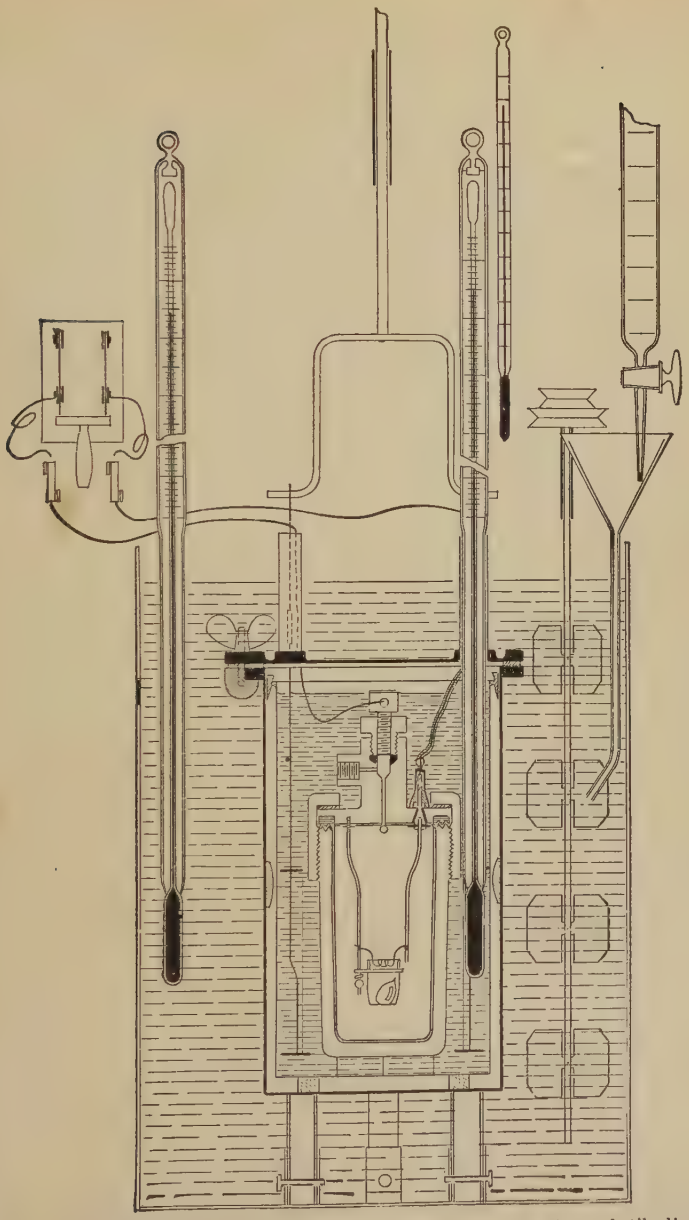


FIG. 50.—Submerged calorimeter, arranged for combustion of a volatile liquid.

to a solution of sodium hydroxide, or by electric heating. A diagram of such a piece of apparatus is shown[1] in Fig. 50, which shows the bomb type of calorimeter arranged for burning a volatile liquid.

The material to be burned is placed in a glass receptacle of very thin walls in a platinum crucible suspended in a heavy steel bomb, lined with gold to prevent any chemical action taking place upon it. The lid is screwed on the bomb, it is filled with oxygen under considerable pressure, and the bomb is closed by the screw valve at its top. The bomb is then placed in the calorimeter (the inner vessel of water) and this is put in another vessel slightly larger than the calorimeter, and closed by a water-tight cover having two outlet tubes for a thermometer and the stirring mechanism. All of this apparatus is submerged in a large tank of sodium hydroxide solution in which are an efficient stirrer and another thermometer, shown at the left. The inner vessel is stirred by a perforated disc moved up and down by the Y-shaped rods shown at the top of the diagram; and the outer bath is stirred by paddles shown at the right until the whole system is at the same temperature.

Upon closing the electric switch, the tiny iron wire shown at the top of the platinum crucible is burned out, its molten products fall on the glass bulb and break it, thus igniting its contents and burning them completely by means of the excess oxygen present. The heat liberated causes a rise in temperature which is indicated on the thermometer reaching to the inner vessel; and a parallel rise in temperature of the outside vessel is produced by adding strong sulfuric acid from a buret at the required rate. Since the outer bath is always kept at the same temperature as the calorimeter within it, there is no exchange of heat between them, and all of the heat of reaction is used to change the temperature of the calorimeter itself. There is thus no heat-loss correction to be made, and the total heat effect is the product of temperature change and heat capacity of the calorimeter. From preliminary experiments, the heat capacity of the calorimeter bomb is determined, and it is immersed in a measured quantity of water. Thus all the data needed for computing the heat effect are at hand, and since a weighed quantity of substance was burned, the heat effect per formula weight is readily computed.

Heat effects for reactions taking place in solutions may be determined in the same way, substituting for the bomb a thin platinum vessel containing one solution. The other solution is discharged into this vessel from a pipet immersed in the calorimeter, in order that the solutions may be at the same temperature when they are mixed for the reaction.

First Law of Heat.—This law is also called the first law of thermodynamics, or the law of conservation of energy. In its

[1] The author is indebted to Prof. T. W. Richards of Harvard College for this diagram of his latest type of submerged calorimeter.

various forms it may state that energy cannot be created or destroyed, but only changed from one form into another; or that the conversion of one kind of energy into another always takes place without loss in the total energy. It follows from this law that the total energy absorbed by a system on changing from one state to another is independent of the manner in which this change is brought about, so long as the same final state is reached from the given initial state, for if the energy absorbed by one path was less than by another, the change in state could be brought about by the process absorbing the greatest energy, reversed by a path absorbing less energy, and an excess of energy would have been gained within the system, which is contrary to the law as stated.

It also follows from this law that the total energy absorbed in a chemical change is evolved when the change is reversed, for if this were not true, a given change could be reversed with less energy than that given up by the first change, and energy would have been created in the cycle. The heat absorbed by any substance when it is heated is evolved completely when this substance is cooled to the original temperature while the original path is retraced. Another way of stating this fact is that "the energy content of a system (any combination of matter) depends only on the conditions under which it exists."

Energy Content and Heat Content.—We have no way of determining the total quantity of energy associated with any system, but only changes in its energy content. Thus if a system undergoes a given change by which it absorbs an amount of energy ΔE, we say that this is the increase in its energy content; or we may write

$$\Delta E = E_2 - E_1,$$

where E_2 and E_1 designate, respectively, the unknown energy contents of the system after the change and before the change. A change in the energy content will also take place if a system does work upon its surroundings without absorbing an equivalent amount of heat. In general, the increase in energy content for any change in state is the difference between the heat absorbed by it during the change in state and the work performed by it, that is

$$\Delta E = q - w.$$

It is convenient also to define another quantity which may be named the heat content[1] and designated by H such that

$$H = E + pv,$$

where E is the energy content. Since for any given system we may measure p and v but not E, the heat content of a system is also not capable of measurement. For any system we may write

$$H_1 = E_1 + p_1v_1,$$

and after this system has undergone some change we may write

$$H_2 = E_2 + p_2v_2$$

and by subtraction

$$H_2 - H_1 = \Delta H = E_2 - E_1 + p_2v_2 - p_1v_1.$$

This equation describes the change in heat content of the system which is associated with the change in state. If a change in state takes place at constant pressure $\Delta E = q - w$, as defined above, and $p_2v_2 - p_1v_1$ becomes $p(v_2 - v_1)$, which is also equal to w, the work done. Hence ΔH is the heat absorbed by the change in state at constant pressure. It is in this sense that we have already used ΔH in the previous chapters. In this chapter it will be used to denote the heat absorbed by a chemical reaction occurring at constant pressure.

Changes in the State of a System.—To define the state of a system we must describe the quantity and composition of it, the state of aggregation (gas, liquid, or solid) of each of its parts if it is not homogeneous, and give the temperature and pressure. Thus a certain system consists of a mol (342 grams) of sugar and 12 mols (384 grams) of oxygen at 20° and 1 atmosphere pressure. By combustion this system may be changed into 12 mols (528 grams) of carbon dioxide and 11 mols (198 grams) of liquid water at 20° and 1 atmosphere pressure, and a certain quantity of heat will be evolved. It is not necessary that the system remain at 20° during the change, but only that it be brought to 20° when the change is completed. By combustion the system would be raised to a higher temperature, and it would be necessary to take heat away from the system in order to restore the original temperature. The quantity of heat taken away in

[1] The notation in this chapter and the definitions of energy content and heat content are those given by Lewis, *J. Am. Chem. Soc.*, **35**, 1 (1912).

order to restore the original temperature is 1,349,400 cal.; and this represents the loss in heat content for the system. The system composed of carbon dioxide and water is poorer in heat than the system composed of sugar and oxygen by this quantity. This is called the decrease in heat content of the system attending the change in state.

Heat Capacities and Specific Heats.—One of the simplest changes in state is that which occurs when a homogeneous substance is heated. We have already considered this type of change under the specific heats of the various substances. When a monatomic gas is heated at constant pressure, the heat absorbed is 5.0 cal. per mol per degree (Chapter III); the absorption of heat per degree for diatomic gases is somewhat larger, and increases with the temperature. Thus for HCl, HBr, HI, O_2, N_2, H_2, CO, and NO the molal heat capacity is $6.5 + 0.001T$, the heat absorbed per mol is the integral of $(6.5 + 0.001T)dT$ between the absolute temperatures involved. The molal heat capacity of halogens in the vapor state is larger,[1] and changes with the temperature more rapidly than that of the other diatomic gases; it is given by the expression $(6.5 + 0.004T)$. The integral of this expression between the desired limits gives the heat absorbed when the halogens are heated in the form of vapor at constant pressure.

For more complex molecules the change of heat capacity with the temperature is not uniform, and quadratic or cubic equations must be used to express the results of experiment over a range of temperature. For water vapor and hydrogen sulfide the equation representing molecular heat capacity is

$$C_p = 8.81 - 0.0019T + 0.00000222T^2; \qquad (1)$$

for carbon dioxide and sulfur dioxide it is

$$C_p = 7.0 + 0.0071T - 0.00000186T^2; \qquad (2)$$

and for ammonia gas

$$C_p = 7.5 + 0.0042T; \qquad (3)$$

where T denotes the absolute temperature. To illustrate the

[1] These data are quoted from LEWIS and RANDALL, *J. Am. Chem. Soc.*, **34**, 1128 (1912). In their "Thermodynamics" they give on page 80 a different equation for the halogens, $7.4 + 0.001T$.

use of such equations, let us calculate the heat required to raise a mol of steam from 100 to 150°C.

$$\text{Heat absorbed} = \int_{373}^{423} (8.81 - 0.0019T + 0.00000222T^2)dT$$

$$= \left[8.81(423 - 373) - \frac{0.0019}{2}\left(\overline{423^2} - \overline{373^2}\right) + \frac{0.00000222}{3}\left(\overline{423^3} - \overline{373^3}\right)\right] = 440.5 - 38 + 18 \text{ or } 420 \text{ cal.}$$

It should be remembered that the heat capacity is a temperature function; and that the heat absorbed is an integral of $C_p dT$ between the temperature limits involved.

These data are all for constant pressure; that is, they include the heat equivalent to the work expended in forcing back the atmosphere. As this work is R cal. per degree for ideal gases, the molal heat capacities of actual gases at constant volume are approximately 2 cal. per degree less than those at constant pressure. Thus, $(4.5 + 0.004T)$ for chlorine at constant volume, $(5.0 + 0.0071T - 0.00000186T^2)$ for carbon dioxide at constant volume.

No simple expressions are known for the heat capacities of liquids; they are generally slightly larger than those for the corresponding solids.

The heat capacities of most of the solid elements approach about 6.2 cal. per atomic weight per degree near room temperature; they fall off rapidly at lower temperatures in a way which is not expressible by a simple equation such as that used for gases. Above ordinary temperature the atomic heats of most solids increase slightly.

The heat capacities of solid compounds are roughly equal to the sum of the heat capacities of the elements in them (Kopp's law). Thus the molecular heat capacity of lead iodide is about equal to that of an atomic weight of lead plus that of two atomic weights of iodine, or about 18.6 cal. per formula weight per degree. When solids are formed from elements which are gases at room temperatures, or from the lighter elements which do not conform to Dulong and Petit's law, their molecular heat capacities are somewhat less than those of the compounds formed from heavy elements. But since the difference between the heat capacity of copper and copper oxide is about the same as that between

zinc and zinc oxide or lead and lead oxide, it is possible to assign to gaseous elements a figure which represents the heat capacity of them in their solid compounds. These figures are given on page 101.

Changes in State of Aggregation.—Heats of evaporation have already been considered under Trouton's law on page 86. The heat absorbed in small calories per mol of liquid evaporated at constant pressure is approximately 20 times the absolute boiling point. Large deviations from this rule are often found, and recourse to experiment is necessary when reliable data are required.

The heat of fusion is a quantity for which no general rule similar to Trouton's rule is known.

Thermochemical Equations.—It is convenient to represent the data of thermochemistry by ordinary chemical equations, to which are added terms indicating the heat effects observed. As an example we may take the combustion of sugar mentioned above. This may be expressed, for 20° and 1 atmosphere,

$$C_{12}H_{22}O_{11} + 12O_2 = 12CO_2 + 11H_2O(\text{liq.}); \Delta H = -1{,}349{,}400 \text{ cal.}$$

In these equations, the formula for a substance represents a formula weight of it just as it does in an ordinary chemical equation, the negative sign of the heat-content increase indicates that heat is evolved. Similarly,

$$H_2O(\text{liq.}) = H_2O(\text{gas}); \Delta H = 9700 \text{ cal. at } 100°$$

indicates the absorption of 9700 cal. of heat from the surroundings during the vaporization of a formula weight of water at 100° and 1 atmosphere.

One other point should be made clear; that the thermochemical equation represents a completed reaction. Thus the equation

$$H_2 + I_2(\text{gas}) = 2HI; \Delta H = -1300 \text{ cal. at } 300°$$

does not state that this quantity of heat will be absorbed when a formula weight of hydrogen and one of iodine are brought together at 300°, for the reaction reaches a state of equilibrium, such that no more hydrogen iodide is formed, when there are substantial quantities of both hydrogen and iodine remaining. The equation states that when *two formula weights of hydrogen iodide are formed* at 300°, −1300 cal. of heat are absorbed. The

excess of reacting substances remains unchanged and so does not absorb heat. Thus approximately this quantity of heat would be absorbed if one formula weight of iodine and 100 mols of hydrogen were brought together, for then the reaction would be substantially complete.

Tables of data usually list latent heats of evaporation as positive, and heat is absorbed during this change; but the heat of a chemical reaction is given as positive when heat is lost from the reacting system. Since it is the system which is interesting to the physical chemist, however, we shall call heat absorbed during a reaction positive, just as heat absorbed during evaporation has been called positive. Thus, our ΔH is the negative of the "heat of reaction" commonly listed and in place of writing

$$H_2 + \tfrac{1}{2}O_2 = H_2O(\text{liq.}) + 68{,}400 \text{ cal.}$$

in which a positive sign would correspond to heat lost from a system, we shall write

$$H_2 + \tfrac{1}{2}O_2 = H_2O(\text{liq.}); \Delta H = -68{,}400 \text{ cal.}$$

Moreover, it is the heat *absorbed* by a system which is used in all of the thermodynamic calculations of physical chemistry, and it is best to become accustomed to this usage at the start. The fact that many reactions proceed of themselves with the evolution of heat is designated quite simply by saying that the heat absorbed by the system is negative during this change.

Law of Constant Heat Summation (Law of Hess).—This law states that when a reaction is brought about in steps, the sum of the heat quantities absorbed in all the steps is equal to that which would have been absorbed had the reaction taken place all at once. It is presumed, of course, that if the total change is brought about at a constant pressure, all of the steps are also at constant pressure. This law was announced before the law of conservation of energy was accepted as a universal fact; we now know that it is only a special case of the more general law. It is very useful in calculating the heat effect for reactions which do not take place readily and quickly. Since the data of thermochemistry are otained by the use of a calorimeter, it is clear that exact determinations cannot be made if the reaction proceeds slowly for several hours, for the radiation losses from the calorimeter would lead to uncertainty in the

measured heat quantity.[1] Many reactions take place in one direction only. The law of conservation of energy states that, if the reaction is reversed, the heat which was absorbed in the first case will be evolved in the second. Thus from the reaction

$$H_2 + \tfrac{1}{2}O_2 = H_2O(\text{liq.}); \Delta H = -68{,}400 \text{ cal. at } 20°$$

we are assured that the reverse reaction would absorb 68,400 cal. of heat from the surroundings, even though we are unable to reverse it at 20° and determine the heat quantity directly.

Copper oxide will react with hydrogen to form water. If a mol of hydrogen is passed over hot copper oxide (the reaction proceeds too slowly for measurement at room temperature), the heat effect will differ from the heat of formation of water from hydrogen and oxygen by the amount of energy necessary to separate oxygen from copper oxide.

Let us consider another indirect process involving two formula weights of hydrogen chloride dissolved in $16Aq$ (16 formula weights of water), an atomic weight of iron, and 384 mols of water.[2] First dissolve the iron in strong acid,

$$Fe + 2(HCl.8Aq) = FeCl_2.16Aq + H_2; \Delta H_1 = -20{,}550 \text{ cal.}$$

Then add water to the solution,

$$FeCl_2.16Aq + 384Aq = FeCl_2.400Aq; \Delta H_2 = x \text{ cal.}$$

This same process may be carried out by first adding water to the strong acid, then dissolving the iron in diluted acid. The thermochemical equations are

$$2(HCl.8Aq) + 384Aq = 2(HCl.200\,Aq); \Delta H_3 = -2660 \text{ cal.}$$
$$Fe + 2(HCl.200\,Aq) = FeCl_2.400\,Aq + H_2; \Delta H_4 = -20{,}800 \text{ cal.}$$

The same total change in state has been brought about, for at first we had iron, strong acid, and water, and in the final system we have hydrogen and dilute ferrous chloride. According to the law of conservation of energy, the same total energy change is involved, and hence we may calculate the heat of dilution of ferrous chloride, x, since

$$\Delta H_1 + \Delta H_2 = \Delta H_3 + \Delta H_4,$$

[1] Barry, *J. Am. Chem. Soc.*, **42**, 1295, 1921 (1920), has developed a calorimeter well suited to measuring heats of slow reactions, but the quantity of data so far obtained is very slight.

[2] Richards, Rowe, and Burgess, *J. Am. Chem. Soc.*, **32**, 1176 (1910).

or, on substituting the numerical values,

$$-20{,}500 + x = -2660 - 20{,}800$$

whence $x = -2910$ cal.

Heats of Reaction at Constant Pressure and at Constant Volume.—Two methods of procedure are followed in calorimetric work, and it is convenient to correct the values obtained by one procedure to those which would have been obtained had the other procedure been employed. Thus when iron is dissolved in acid in an open vessel, the hydrogen formed must force back the atmosphere to make room for itself, thereby doing work. If the reaction had been carried out in a strong closed bomb, a pressure of hydrogen would have been built up and no work would have been performed. Later when the bomb is opened, hydrogen rushes out, driving back the atmosphere as it does so, and performs work (at the same time absorbing some of the heat originally given to the surroundings) so that the total heat absorbed is the same as during the constant-pressure process. The work done is $p(v_2 - v_1)$ in the first process where hydrogen was evolved at 1 atmosphere, and is zero for the constant-volume process, as the work done when the bomb is opened is not considered part of the calorimetric process. An amount of heat equivalent to this work done is absorbed in the constant-pressure process, but not in the constant-volume process. The heat absorbed during the reaction at 1 atmosphere pressure is ΔH, but since no work is done by the reaction which takes place at constant volume, the total energy absorbed is ΔE. By definition these quantities differ from one another by Δpv, that is,

$$\Delta H = \Delta E + p(v_2 - v_1). \tag{4}$$

In this expression v_2 is the volume of a mol of hydrogen plus that of a mol of dissolved ferrous chloride, and v_1 is the volume of the iron and acid from which it was formed. There is only a slight change in the volume of the solution, and the volume of the iron may be neglected in comparison with that of the gas. The work term then becomes practically pv_2, which from the ideal gas equation is RT. Since the value of R is 1.99 cal., the correction term is at once available in calories, and the difference at 20° is $1.99 \times 293 = 586$ cal. of heat absorbed per mol of gas generated. This should be rounded to 600 cal., since otherwise

upon addition we would write down a larger number of significant figures than the experimental work justifies.

For reactions involving only solids and liquids the difference between heats of reaction at constant volume and at constant pressure usually need not be taken into account. For reactions in which gases are involved, the increase in volume is the *increase* in the number of *mols of gas* during the reaction. In general,

$$\Delta H = \Delta E + \Delta nRT, \qquad (5)$$

where Δn is the increase in the number of *mols of gas* which takes place when the reaction occurs. For the combustion of carbon monoxide,

$$2CO + O_2 = 2CO_2; \Delta H = -136{,}000 \text{ cal., and } \Delta n = -1,$$

so that the heat absorbed during the combustion of two mols of CO in a closed vessel would be less than in the open air by the amount RT or 600 cal.

All the data given in this chapter are for the constant pressure of 1 atmosphere unless otherwise stated.

Heats of Combustion.—The heats of combustion for a large number of organic compounds have been determined carefully, and they are used for another purpose which is explained in the next paragraph. Many organic substances do not burn readily in air; others (such as naphthalene) are not completely changed to water and carbon dioxide when burned in air. It is therefore customary to determine these heats of combustion in a closed calorimeter with oxygen under considerable pressure. Data for almost all of the common organic compounds may be found in Landolt-Börnstein's tables, or in the translation of Thomsen's "Thermochemistry," but it should be noted in referring to these data that they employ the opposite convention from ours, and list the heat evolved during a reaction as positive. Many of these heats of combustion were determined before the highest calorimetric precision had been developed, and the data are often in error by 1 or 2 per cent. For approximate calculations, this is not serious; but it is a great disadvantage when accurate data are desired. This work is, therefore, being given careful scrutiny by modern chemists; much of it has been repeated under more favorable conditions, and accurate heats of combustion are rapidly

becoming available. Table 79 shows some recently determined heats of combustion which are especially accurate.

TABLE 79.—HEATS OF COMBUSTION AT CONSTANT VOLUME[1]

Substance	Heat absorbed per	
	Gram	Formula weight
Sugar	− 3,945	−1,349,400
Benzoic acid	− 6,325	− 771,550
Naphthalene	− 9,624	−1,231,600
Benzene	−10,026	− 781,850
Toluene	−10,167	− 935,230
$C_6H_5C_2H_5$	−10,273	−1,089,000
ter-Butyl benzene	−10,446	−1,399,800
Xylene (*o* and *m*)	−10,277	−1,089,000
Cyclohexanol ($C_6H_{11}OH$)	− 8,892	− 899,300
Di-isoamyl	−11,356	−1,612,600
Methyl alcohol	− 5,333	− 170,610
Ethyl alcohol	− 7,110	− 327,040
Propyl alcohol	− 8,044	− 485,800
Butyl alcohol	− 8,626	− 638,330
Isobutyl alcohol	− 8,610	− 637,144

Calculation of Heats of Combustion.—The mechanism of combustion of hydrocarbon compounds consists in severing bonds between carbon and carbon, or between carbon and hydrogen, and in establishing unions between carbon and oxygen, and between hydrogen and oxygen. Several simple relations between the heat of combustion and the number and character of bonds severed have been discovered. For example, Thornton[2] states that the formal heat of combustion of a saturated hydrocarbon is approximately −52,700 cal. absorbed for each atomic weight of oxygen required to burn it. Ethane requires seven atomic weights of oxygen per mol of it burned; the heat absorbed during combustion should, therefore, be $7 \times -52{,}700$ or −368,900 cal., and this is in agreement with experiment. In Table 80 are given

[1] RICHARD and DAVIS, *J. Am. Chem. Soc.*, **42,** 1614 (1920); *cf.* **37,** 993 (1915). For other data, see SWIETOSLAWSKI, *J. Am. Chem. Soc.*, **42,** 1092 (1920).

[2] THORNTON, *Phil. Mag.*, **33,** 196 (1917).

the heats of combustion determined experimentally for several compounds, and in the last column the heat of combustion divided by the number of atomic weights of oxygen used.

TABLE 80.—HEAT OF COMBUSTION

Compound	Heat absorbed on combustion	Heat absorbed per atomic weight of oxygen
Methane	−210,800	−52,700
Ethane	−369,000	−52,700
Propane	−527,500	−52,700
Trimethylmethane	−685,200	−52,700
Tetramethylmethane	−844,800	−52,800
Di-isopropyl	−996,600	−52,500

TABLE 81.—HEATS OF COMBUSTION

Compound	Bonds severed	Calculated heat absorbed in combustion	Measured heat absorbed in combustion	Per cent error in calculated value
Ethylene	4C—H + 1C=C	−332,600	−332,100	0.2
Methyl formate	4C—H + 2C—O	−240,800	−240,600	0.1
Acetic anhydride	6C—H + 2C—C + 2C—O	−452,000	−459,500	1.6
Ether	10C—H, 2C—C 2C—O	−662,800	−657,900	0.8
Methyl acetate	6C—H, 1C—C, 2C—O	−399,100	−398,400	0.5
Methyl isobutyrate	10C—H, 3C—C, 2C—O	−715,700	−715,500	0.0
Acetylene	2C—H, C≡C	−308,600	−313,000	1.4

This rule applies only to saturated hydrocarbons. A more general one[1] is stated in terms of the number and character of the bonds severed during combustion. Expressed in thousands of calories, the molal heat of combustion is the sum of −52.7 times the number of C—H bonds; −52.9 times the number of C—C bonds;[2] −121.8 times the number of C=C; −203.2 times the

[1] REDGROVE, *Chem. News*, **116**, 37 (1917).

[2] SWIETOSLAWSKI, *J. Am. Chem. Soc.*, **42**, 1312 (1920), gives −53.72 for a C—C bond and −52.25 for each C—H. Thus the change in molal heat of combustion in ascending any homologous series is two C—H bonds plus one C—C, or −157.8 large cal.; RICHARDS, *J. Am. Chem. Soc.*, **42**, 1616 (1920), gives −153.5 large cal. for the average difference in heat corresponding to each CH_2 group added.

number of C≡C bonds; and −15.0 times the number of C—O bonds. Since the C=O bond persists in CO_2 and is unchanged by combustion, no heat is absorbed on account of it. The reliability of this rule is illustrated by Table 81. The agreement leaves something to be desired, but in case no data are available, rough values calculated from these rules will often be of considerable service.

Heats of Formation.—By means of the law that the total energy change associated with a change in the state of a system is independent of the manner in which this change is brought about, we are able to compute the heats of formation of compounds from their elements, even in cases where this direct synthesis is not possible in the calorimeter. For example, let us write the equation for the formation of benzoic acid from its elements, and a second equation for the complete combustion of benzoic acid into carbon dioxide and water.

$$7C + 3H_2 + O_2 = C_6H_5COOH; \Delta H = x \text{ cal.}$$

$$C_6H_5COOH + 7\tfrac{1}{2}O_2 = 7CO_2 + 3H_2O \text{ (liq.)}; \Delta H = -770{,}000 \text{ cal.}$$

$$7C + 3H_2 + 8\tfrac{1}{2}O_2 = 7CO_2 + 3H_2O(\text{liq.}); \Delta H = -881{,}400$$

Under these reactions is written the sum of them, which is the combustion of carbon and hydrogen. The heat of this last reaction was calculated from the equations

$$C + O_2 = CO_2; \Delta H = -96{,}600 \text{ cal. and}$$

$$H_2 + \tfrac{1}{2}O_2 = H_2O \text{ (liq.)}; \Delta H = -68{,}400 \text{ cal.,}$$

by multiplying the first one by 7 and the second one by 3, and adding, which gives $\Delta H = -881{,}400$. The formation of benzoic acid plus its combustion absorbs the same amount of heat as the direct combustion of the elements, whence $x - 770{,}000 = -881{,}400$, or

$$7C + 3H_2 + O_2 = C_6H_5COOH; \Delta H = -111{,}400 \text{ cal.}$$

In many cases this indirect method is not needed, as the elements combine directly and readily in the calorimeter. Some examples are quoted for reference and as data for use in solving the problems at the end of the chapter.

TABLE 82.—HEATS OF FORMATION OF CHEMICAL COMPOUNDS[1]

$Pb + I_2 = PbI_2; \Delta H = -41{,}850$ cal.
$Ag + I = AgI; \Delta H = -15{,}100$ cal.
$Pb + Cl_2$ (gas) $= PbCl_2; \Delta H = -85{,}700$ cal.
$Pb + Br_2$ (liq.) $= PbBr_2; \Delta H = -66{,}350$ cal.
$Ag + \frac{1}{2} Cl_2$ (gas) $= AgCl; \Delta H = -30{,}410$ cal.
$2Na + S = Na_2S; \Delta H = -89{,}700$ cal.
$Na_2S + Aq = Na_2S$ (dissolved); $\Delta H = -15{,}500$ cal.
$2K + S = K_2S; \Delta H = -87{,}100$ cal.
$K_2S + Aq = K_2S$ (dissolved); $\Delta H = -22{,}700$ cal.
$H_2 + Cl_2 = 2HCl$ (gas); $\Delta H = -44{,}000$ cal.
HCl (gas) $+ 200\,Aq = HCl.200Aq; \Delta H = -17{,}300$ cal.
$Na + \frac{1}{2}Cl_2 = NaCl; \Delta H = -97{,}900$ cal.
$H_2 + S = H_2S; \Delta H = -2730$ cal.

$K + \frac{1}{2} Br_2$ (liq.) $= KBr; \Delta H = -95{,}310$ cal.
$\frac{1}{2} Br_2$ (gas) $= \frac{1}{2} Br_2$ (liq.); $\Delta H = -3750$ cal.
$K + \frac{1}{2} Br_2$ (gas) $= KBr; \Delta H = -99{,}060$ cal.

$K + \frac{1}{2} I_2$ (solid) $= KI; \Delta H = -80{,}130$ cal.
$\frac{1}{2} I_2$ (gas) $= \frac{1}{2} I_2$ (solid); $\Delta H = -7400$ cal.
$K + \frac{1}{2} I_2$ (gas) $= KI; \Delta H = -87{,}530$ cal.

$K + \frac{1}{2} Cl_2$ (gas) $= KCl; \Delta H = -105{,}610$ cal.

$Ca + \frac{1}{2}O_2 = CaO; \Delta H = -151{,}400$ cal.
$Sr + \frac{1}{2}O_2 = SrO; \Delta H = -139{,}400$ cal.
$Ba + \frac{1}{2} O_2 = BaO; \Delta H = -126{,}400$ cal.

Certain regularities in heats of formation have been pointed out[2] in connection with the groups in the periodic table, of which examples are quoted above. The molal heat of formation of strontium oxide is very nearly the average of the molal heats of formation of calcium oxide and barium oxide. Similarly, the molal heats of formation of bromides are about the average of the heats of formation of corresponding chlorides and iodides, after due allowance has been made for the fact that bromine is a liquid and iodine is a solid. For example, the heat of formation of calcium iodide from calcium and iodine vapor is the sum of the equations

$Ca + I_2$ (solid) $= CaI_2; \Delta H = -127{,}400$ cal.
I_2 (gas) $= I_2$ (solid); $\Delta H = -14{,}800$ cal.
$Ca + I_2$ (gas) $= CaI_2; \Delta H = -142{,}200$

[1] Partly from BRAUNE and KOREF, *Z. anorg. Chem.*, **87**, 175 (1914).
[2] MIXER, *Ann. J. Sci.*, **37**, 519 (1914).

The heat absorbed when a mol of calcium chloride forms is −190,400 cal., and the average of these heats should be about the heat of formation of calcium bromide from calcium metal and bromide vapor. This average is −166,300 cal., the experimental value is

$$\begin{aligned} Ca + Br_2\ (liq.) &= CaBr_2;\ \Delta H = -154{,}200\ cal. \\ Br_2\ (gas) &= Br_2\ (liq.);\ \Delta H = -7500\ cal. \\ \hline Ca + Br_2\ (gas) &= CaBr_2;\ \Delta H = -161{,}700. \end{aligned}$$

The calculated heat of formation is about 3 per cent in error, which illustrates the general accuracy of this rule of average heats.

Heat Content of Compounds at Constant Pressure.—The reaction $2Na + S = Na_2S$; $\Delta H = -89{,}700$ cal. shows that the heat content of the compound is less than that of the elements from which it was formed by 89,700 cal. There is no way of determining the total heat content of a substance, but it is customary to consider the heat content of each element as zero and refer compounds to this standard. Then the heat content of sodium sulfide is −89,700 cal., referred to its elements, since this amount of heat was absorbed during its formation. Similarly, the heat content of hydrogen chloride is 22,000 cal. less than that of its constituent elements, and the heat content of $HCl.200Aq$ is −37,300 cal., referred to the elements and to the solvent water as zero. This gives a ready means of calculating the heat of a reaction in terms of the heats of formation of the substances involved in it, for in the chemical equation we need only substitute the heat absorbed upon formation for each substance and solve for the remaining term, which will cause the equation to balance. For example,

$$\begin{aligned} Na_2S + 2HCl\ (gas) &= 2NaCl + H_2S\ (gas);\ \Delta H = x\ cal. \\ -89{,}700 + 2(-22{,}000) &= 2(-97{,}900) + (-2730);\ \Delta H = x. \end{aligned}$$

The heat content of the substances on the left is −133,700; that on the right is −198,530, when the heat-content decrease during the reaction is 64,830 cal., or $\Delta H = -64{,}830$. This same result might have been attained by adding together in appro-

priate way the thermochemical equations from which the heats of formation were taken, as follows:

$$\begin{aligned}
Na_2S &= 2Na + S; & \Delta H &= -89{,}700 \text{ cal.} \\
2HCl &= H_2 + Cl_2; & \Delta H &= +44{,}000 \text{ cal.} \\
2Na + Cl_2 &= 2NaCl; & \Delta H &= -195{,}800 \text{ cal.} \\
H_2 + S &= H_2S; & \Delta H &= -2730 \text{ cal.} \\
\hline
Na_2S + 2HCl &= H_2S + 2NaCl; & \Delta H &= -64{,}830 \text{ cal.}
\end{aligned}$$

Heat of Solution.—Some substances dissolve in water with the absorption of heat (ammonium salts, many potassium compounds), but the majority of solids and liquids, and all gases, evolve heat when they dissolve in water. The heat effect depends on the quantity of water used per mol of dissolved substance up to a certain limit, which limit may be determined by dilution experiments. For example, the solution of 1 mol of hydrogen chloride in 250 c.c. of water absorbs −16,500 cal., the addition of 250 c.c. more water absorbs −450 cal., the addition of 500 more (to make a total of 1 liter) absorbs −300 cal. more, the dilution with another liter of water only −150 cal., and further addition of water causes no appreciable heat effect. Hence the solution of 1 mol of hydrogen chloride in 2 liters of water absorbs as much heat as its solution in a larger quantity of water. Such a solution is written $HCl.Aq$; one containing less water should be written with the number of gram-molecules of water indicated, as $HCl.27.75Aq$ for a two-molal solution, $HCl.55.5Aq$ for a molal solution, etc. As thermochemical equations, the heats of dilution are written

$$HCl.20Aq + 80Aq = HCl.100Aq; \quad \Delta H = -480 \text{ cal.}$$

It has been found upon mixing solutions of salts which are highly ionized that there is practically no heat effect attending the formation of the new salts, provided these do not precipitate from solution. The heat effect of $NaCl.Aq + KNO_3.Aq = KCl.Aq + NaNO_3.Aq$ is very small, but the heat effect of $AgNO_3.Aq + NaCl.Aq = AgCl$ (solid) $+ NaNO_3.Aq$ is considerable, owing to the formation of a solid substance from constituents existing in solution.

Heat of Neutralization.—The average heat effect when a dilute ionized acid is added to a dilute ionized base is −13,800 cal.

absorbed per mol of water formed. That is, the heat absorbed when hydrogen ion and hydroxyl ion combine to form water is $-13{,}800$ cal. per mol. The case is quite different with slightly ionized substances such as weak acids and bases; but it is often impossible in calorimetric experiments to dilute these solutions to such concentrations that they are largely ionized. Substantially complete ionization may be brought about in another way, however, by removing one of the products of ionization. The reaction

$$NH_4OH = NH_4^+ + OH^-$$

proceeds to completion in the presence of an acid which supplies hydrogen ions to combine with the hydroxyl ions as soon as they are formed, and the net effect as shown by the equations

$$NH_4OH = NH_4^+ + OH^-;\ \Delta H = x \text{ cal.}$$
$$H^+ + OH^- = H_2O;\ \Delta H = -13{,}800 \text{ cal.}$$
$$NH_4OH + H^+Cl^- = H_2O + NH_4^+Cl^-;\ \Delta H = -12{,}300 \text{ cal.}$$

is readily carried out by mixing ammonium hydroxide with hydrochloric acid in a calorimeter. And since $-13{,}800 + x = -12{,}300$, $x = +1500$ cal. Such effects are not observed during neutralization of strong electrolytes as shown by the following reactions:[1]

$$HCl.Aq + KOH.Aq = KCl.Aq + H_2O;\ \Delta H = -13{,}930 \text{ cal.}$$
$$HCl.Aq + NaOH.Aq = NaCl.Aq + H_2O;\ \Delta H = -13{,}680 \text{ cal.}$$
$$HBr.Aq + NaOH.Aq = NaBr.Aq + H_2O;\ \Delta H = -13{,}750 \text{ cal.}$$
$$HI.Aq + NaOH.Aq = NaI.Aq + H_2O;\ \Delta H = -13{,}680 \text{ cal.}$$
$$HNO_3.Aq + NaOH.Aq = NaNO_3.Aq + H_2O;\ \Delta H = -13{,}690 \text{ cal.}$$
$$HNO_3.Aq + KOH.Aq = KNO_3.Aq + H_2O;\ \Delta H = -13{,}870 \text{ cal.}$$
$$HNO_3.Aq + TlOH.Aq = TlNO_3.Aq + H_2O;\ \Delta H = -13{,}690 \text{ cal.}$$

All of these reactions are essentially the union of hydrogen ion with hydroxyl ion, since the negative ion of the acid and the positive ion of the base constitute the ions of the salt formed. The differences are not due to errors of experiment, but the variations are small enough to be overlooked for the present, and we may write as a summary of all these reactions the rounded value

$$H^+ + OH^- = H_2O;\ \Delta H = -13{,}800 \text{ cal. at } 20°.$$

[1] WÖRMANN, *Ann. Physik*, **18**, 775 (1905).

Heat of Neutralization and Temperature.—The average value −13,800 cal. stated above does not apply to other temperatures, as will be seen from Table 83.[1]

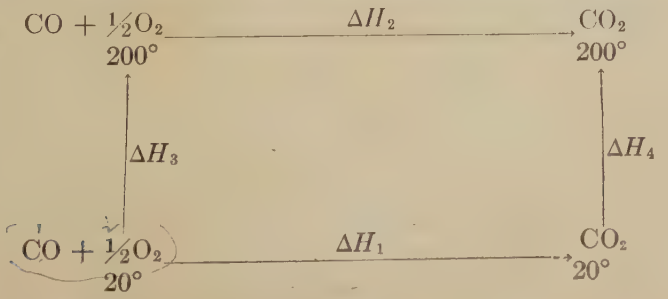
TABLE 83.—HEAT OF NEUTRALIZATION AT DIFFERENT TEMPERATURES

Temperature (degrees)	Salt formed by neutralization			
	KCl	NaCl	KNO_3	$NaNO_3$
0	−14,740	−14,590		
6	−14,460	−14,350	−14,430	−14,360
18	−13,930	−13,680	−13,870	−13,700
32	−13,160	−12,960	−13,100	−12,920

Heat of Reaction and Temperature.—Consider a reaction which may occur at two temperatures T_1 and T_2, and let the heat absorbed by the reaction be ΔH_1 at T_1 and ΔH_2 at T_2. The reaction may occur at T_1, after which the products of reaction are heated to T_2, or the reacting substances may be heated to T_2 and the reaction allowed to take place at that temperature. The total change in heat content in these two steps must be the same, for in each case the initial state of the system consists of the reacting substances at T_1; and its final state consists of the reaction products at the temperature T_2. Let us take as an illustration the combustion of carbon monoxide with oxygen at constant pressure. At 20° this reaction is represented by the thermochemical equation

$$CO + \tfrac{1}{2}O_2 = CO_2;\ \Delta H_1 = -68{,}000 \text{ cal.},$$

and it is desired to calculate the heat absorbed in this reaction at 200°. The following diagram shows the method of calculation:



[1] WÖRMANN, *Ann. Physik*, **18**, 775 (1905).

We shall consider the heat absorbed by the system in each of the steps. Since $\Delta H_3 + \Delta H_2$ correspond to one path between the initial state of the system (1CO and $\frac{1}{2}O_2$ at 20°) and the final state of the system ($1CO_2$ at 200°), and $\Delta H_1 + \Delta H_4$ are for another path by which the same change of state occurs,

$$\Delta H_3 + \Delta H_2 = \Delta H_1 + \Delta H_4.$$

This is required by the first law of heat, since if it were not true the change of state could be brought about by one path, reversed by the path absorbing the smaller quantity of heat, thus restoring the system to its original state, and creating energy within the system. This is impossible in the light of all experience. Here ΔH_1 is known, and ΔH_3 and ΔH_4 may be calculated from specific heat data. For the first process we must heat 1.5 mols of diatomic gas from 20 to 200°, absorbing the quantity of heat

$$\Delta H_3 = 1.5 \int_{293}^{473} (6.5 + 0.001T)dT = 1858 \text{ cal.}$$

For ΔH_4, 1 mol of carbon dioxide is heated through the same temperature range.

$$\Delta H_4 = \int_{293}^{473} (7.0 + 0.0071T - 0.00000186T^2)dT = 1708 \text{ cal.}$$

We may now calculate the heat effect at the higher temperature.

$$1858 + \Delta H_2 = 1780 + \Delta H_1;$$

whence $\Delta H_2 = -68{,}150$. Combustion of a mol of carbon monoxide at 200° absorbs $-68{,}150$ cal. of heat.

The general method of calculating a heat effect at one temperature from the value of it at another temperature is that indicated above. There should be formulated first the changes in heat content corresponding to the reactions at two different temperatures, and then the changes connected with heating the reacting substances or the reaction products from one temperature to another, as is done on page 224. If the heat capacity of a system increases during reaction, a smaller quantity of heat will be absorbed in raising the reacting substances to the higher temperature and hence there will be a larger absorption of heat at the higher temperature. This may be expressed by the equation

$$\Delta H_2 - \Delta H_1 = \Delta C_p(T_2 - T_1), \qquad (6)$$

when ΔC_p does not change with the temperature. If the heat capacities are functions of the temperature, as in the illustration just given, the equation is

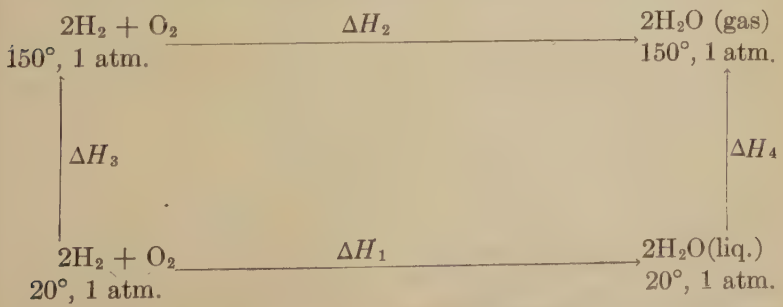
$$\frac{d(\Delta H)}{dT} = \Delta C_p. \tag{7}$$

Before equation (7) can be integrated, each heat capacity must be expressed as a temperature function, ΔC_p obtained by subtraction, and its proper value inserted in the equation. In the example above, C_2 is $7.0 + 0.0071T - 0.00000186T^2$ for 1 mol of CO_2, C_1 is $9.75 + 0.0015T$ for 1 CO and $\frac{1}{2}O_2$, and ΔC_p is, therefore, $-2.75 + 0.0056T - 0.00000186T^2$. Substituting in equation (7) and integrating between the proper limits, we have

$$\Delta H_2 - \Delta H_1 = -\int_{293}^{473}(2.75 - 0.0056T + 0.00000186T^2)dT,$$

whence $(\Delta H_2 - \Delta H_1)$ is -150 cal., and ΔH_2 is $-68{,}150$ cal. as above.

This equation should not be applied in any case where there is a change in the *state of aggregation* of any substance involved upon heating from one temperature to another, for such a change takes place with the absorption of heat at a constant temperature, and cannot be included in the temperature function of specific heats. For example, if liquid water is formed at the lower temperature, and water vapor at the higher one, there is during heating of the reaction products a large absorption of heat when evaporation takes place with no attendant change of temperature. Let us consider the union of hydrogen and oxygen to form water vapor at 150°, to illustrate this point.



Here ΔH_1 plus the change of state indicated by ΔH_4 must absorb

the same quantity of heat as ΔH_3 plus ΔH_2, according to the law of conservation of energy. Now ΔH_1 is $-68{,}400$ cal. per mol of liquid water formed, or $-136{,}800$, and ΔH_4 is the sum of three steps, the value of each of which may be calculated: First heat 2 mols of liquid water from 20° to 100°, absorbing the quantity of heat $2 \times 18 \times 80 = 2880$ cal.; second, evaporate this water at constant pressure, absorbing the heat $2 \times 18 \times 538 = 19{,}400$ cal.; third, heat the water vapor from 100 to 150°, absorbing 420 cal. per mol, as calculated on page 224. The sum of these quantities is 23,120.

Also the heat absorbed by $2H_2 + O_2$ is three times the integral of $(6.5 + 0.001T)$ between the temperatures $T_1 = 293$ and $T_2 = 423$, since 3 mols of a diatomic gas are involved. The value of this integral is 2670 cal. absorbed. Then

$$2670 + \Delta H_2 = 23{,}120 - 136{,}800; \text{ or } \Delta H_2 = -116{,}350 \text{ cal.}$$

The heat absorbed per mol of water vapor formed is thus $-58{,}200$ cal. at 150°. Final results of calculations should be rounded off in this manner, for writing $-58{,}175$ indicates a more exact result than is justified by either calculations or data.

A constant pressure has been assumed throughout these calculations of temperature effect. Similar considerations apply to constant-volume changes. It is only necessary that the same total change of state be produced by each of two paths in order to equate the change of heat content ΔH, or of energy content ΔE by one path to that of another path. Since ΔE is equal to the heat absorbed by a reaction occurring at constant volume, it is usually more convenient to sum the values of ΔE in constant-volume processes.

Calculation of Flame Temperatures.—The maximum temperature of a flame may be calculated by the principles explained in the previous paragraphs. In the oxy-acetylene flame, for example, water vapor and carbon dioxide are formed, and the thermochemical equation is

$$C_2H_2 + 2\tfrac{1}{2}O_2 = 2CO_2 + H_2O; \Delta H = -313{,}000 \text{ cal. at } 20°.$$

If no heat is lost to the surroundings, all of it is available for heating the products of reaction, and the highest temperature attainable with such a flame is the maximum which can be reached by adding 313,000 cal. to 88 grams of carbon dioxide

and 18 grams of liquid water. This temperature follows from the specific heat equations:

$$313{,}000 = 1440 + 9700 + 2\int_{373}^{T}(7.0 + 0.0071T - 0.00000186T^2)\,dT + \int_{293}^{T}(8.81 - 0.0019T + 0.00000222T^2)dT,$$

where 1440 cal. are required to heat a mol of liquid water to 100°, 9700 cal. are required to vaporize it, and the other terms refer to heating a mol of water vapor and two mols of carbon dioxide. Integrated and simplified, this equation is

$$309{,}900 = 24.6T + 0.0017T^2 + 0.0000086T^3.$$

It is not necessary to apply the general solution of a cubic to this problem; a value of T is estimated and substituted into the right-hand side of the equation; if it produces a smaller total than 309,900, the estimate was too low and a higher one should be made. In the present instance, by estimating $T = 5000$ the right-hand side becomes 283,500, and by estimating $T = 5300$ it is 324,500. Hence the maximum temperature reached is between these two absolute temperatures. As considerable heat is always lost to the surroundings, and combustion is not complete when just the theoretical quantity of oxygen is used, it is unlikely that the theoretical maximum will be reached, or approached within a few hundred degrees; and it is therefore unnecessary to estimate the available temperature more closely than this. For most rough calculations of this kind the molal heat capacity of carbon dioxide may be taken as $7.0 + 0.0028T$ and that of water vapor as $8.6 + 0.0030T$ without great error.

In making this calculation it has been assumed that water vapor and carbon dioxide were the only products formed, but if a temperature approaching 5000° is reached, considerable dissociation of the former into hydrogen and oxygen and considerable dissociation of the latter into carbon monoxide and oxygen takes place. These dissociations will absorb heat, thus decreasing that available for raising the temperature of the products of combustion. Such calculations as that here given therefore represent the maximum attainable temperature under the most favorable conditions, and are always higher than the temperatures actually reached.

Questions

1. The heat absorbed during the combustion of a gram of naphthalene ($C_{10}H_8$) at 20° is −9612 cal. Calculate the heat of formation of a mol of it.

2. Calculate the heat required to raise 50 grams of bromine vapor from 63 to 150°C. *Ans.* 220 cal.

3. Calculate the heat evolved upon cooling a mol of steam at constant pressure from 200 to 100°. *Ans.* 840 cal.

4. How much heat will be required to raise a cubic foot of air (28 liters) from 0 to 100° at constant volume? At constant pressure?

5. The heat of solution of aluminum in HCl.200Aq is $-127{,}060$ cal. absorbed per atomic weight; in HCl.20Aq it is $-126{,}000$ cal. The heat of dilution of hydrochloric acid from HCl.20Aq to HCl.200Aq is -500 cal. absorbed per mol of acid. Calculate the heat of dilution of aluminum chloride solution.

6. The heat of solution of magnesium in HCl.200Aq is $-110{,}200$ cal. per atomic weight. Calculate the change in heat content for the reaction $3Mg + 2AlCl_3.Aq = 3MgCl_2.Aq + 2Al$.

7. The heat of evaporation of water at 100° and constant pressure is 538.9 cal. per gram. Calculate the heat of evaporation at 150°. Over this small range of temperature the molal heat capacity of water vapor may be taken as $8.6 + 0.003T$.

8. When a gram of alcohol is burned at constant pressure, 7100 cal. are *evolved*. Calculate the heat absorption per mol at constant volume.

9. Calculate the heat of formation of a mol of alcohol at constant pressure. Its heat of combustion is -7100 cal. absorbed per gram.

10. The heat of evaporation of water at constant pressure (1 atmosphere) is 538.9 cal. per gram at 100°. Calculate the heat absorbed when a mol of water evaporates at 100° into an exhausted space, so that no work is done.

11. Anthracene ($C_{14}H_{10}$, mol. wt. 178) melts at 216°, and absorbs 38.7 cal. per gram during fusion. Calculate the heat absorbed if 10 grams of liquid anthracene are cooled to 150° and solidification is allowed to take place there. The specific heat of the liquid is 0.509, that of the solid is $0.28 + 0.0007t$, where t is the Centigrade temperature.

12. Calculate the heat evolution per gram of water which is undercooled to $-15°$ and there solidified. The latent heat of fusion is 79 cal. per gram at zero, and the specific heat of ice is half that of liquid water.

13. Compute the heat of combustion of octane by Thornton's rule and by Redgrove's rule, and the percentage error of each. The experimental value is $-1{,}302{,}000$ cal. absorbed per molecular weight (114.1 grams).

14. Estimate the heat of combustion of trimethylethylene by Redgrove's rule, and compare it with the result of experiment, $-795{,}800$ cal. per mol.

15. Carbon monoxide may be manufactured by passing a mixture of oxygen and carbon dioxide over hot carbon. Since the oxidation of carbon evolves heat and the reduction of carbon dioxide by carbon absorbs heat, there is a mixture of oxygen and CO_2 which can be passed over carbon at 900°, where it will be changed to practically pure carbon monoxide without changing the temperature of the carbon bed. Calculate the heat of each reaction at 900°; and the composition of the gas mixture which will cause no change in temperature in the coke bed. At 20° the combustion of carbon absorbs $-97{,}000$ cal. per mol of CO_2 formed, the combustion of a mol of CO absorbs $-68{,}000$ cal., the atomic heat capacity of carbon may be taken as 4.0 cal. over the whole temperature range, the molal heat capacities of oxygen and CO are $6.5 + 0.001T$, and that of carbon dioxide may be taken as $7.0 + 0.0028T$. Assume that the gas enters and leaves at 900°.

16. At 25° $H_2 + I_2$ (solid) = 2HI; ΔH = 12,200 cal.; between 25 and 400° the average specific heat capacity of hydrogen is 3.5 cal. per degree, that of HI is 0.055, and that of iodine vapor 0.034 cal. per degree. Assume the heat capacity of solid iodine to conform to the law of Dulong and Petit; the heat of sublimation of iodine at 75° is 56 cal. per gram. Calculate the heat absorbed by the reaction $H_2 + I_2$ (gas) = 2HI at 400°.

17. Estimate the heat of formation of HBr from its elements at 500°. The boiling point of bromine is 59°, its latent heat of vaporization is about 40 cal. per gram. Estimate the heat capacity of liquid bromine from the law of Dulong and Petit (which, however, applies strictly only to solids). The following data are needed:

$$H_2 + Br_2 \text{ (liq.)} + Aq = 2HBr.Aq; \Delta H = -56{,}600 \text{ cal. at } 20°.$$
$$HBr + Aq = HBr.Aq; \Delta H = -19{,}900 \text{ cal. at } 20°.$$

The molal heat capacity C_p for hydrogen and HBr is $6.5 + 0.001T$ and for bromine vapor $C_p = 6.5 + 0.004T$. Assume 1 atmosphere throughout.

18. The heat absorbed upon solution of 1 mol of hydrogen iodide in $100Aq$ is −19,200 cal., the heat of solution of calcium oxide in water is −18,300 cal., and the heat of solution of calcium iodide is −27,700 cal. Calculate the heat absorbed upon adding a mol of calcium oxide (solid) to a large quantity of HI.$100Aq$. The other data needed are stated in the text.

19. When a mol of 0.1 formal H_3PO_4 is neutralized with sodium hydroxide, the heat absorbed is −14,800 cal. Phosphoric acid is about 30 per cent ionized into H^+ and $H_2PO_4^-$. The heat absorbed in the ionization of water is 13,800 cal. per mol. Calculate the heat absorbed per mol of phosphoric acid ionized.

20. Calculate the heat absorbed by the reaction $C_{12}H_{22}O_{11} + H_2O = 4C_2H_5OH + 4CO_2$. The heats of formation are −68,400 for water and −96,600 for CO_2. The heat absorbed on combustion of alcohol is −326,500 cal. per mol, and that for sugar is −1,354,000 cal. per mol.

21. Calculate the heat absorbed by the reaction $C + H_2O = CO + H_2$ at 800°. The heat absorbed in the formation of carbon monoxide from carbon and oxygen at 20° is −29,000 cal. per mol, the atomic heat of carbon is 4 cal. per degree and the heat capacity of water vapor may be taken as $8.6 + 0.003T$. The other necessary data are given in the previous problem.

22. (*a*) Calculate the heat of formation of silver chloride at 150° and constant pressure. Its heat of formation is −29,000 cal. absorbed per mol at 15°; the atomic heat capacity of silver is 6.0; the molal capacity of AgCl is 14.3 and that for chlorine is $7.4 + 0.001T$. (*b*) Calculate the heat absorbed during the formation of AgCl at 15° and *constant volume.*

CHAPTER VIII

EQUILIBRIUM IN HOMOGENEOUS SYSTEMS

One of the most important problems of physical chemistry has been the study of the conditions which govern the *extent* to which reactions take place. Most of the familiar reactions of inorganic chemistry, especially those of analytical chemistry, have been useful because they go forward until one or more of the reacting substances is completely exhausted. In the gaseous reactions $H_2 + Cl_2 = 2HCl$ and $2H_2 + O_2 = 2H_2O$ as ordinarily carried out, there is after the reaction no appreciable quantity of the reacting substances remaining if they were put together in equivalent quantity. If an excess of hydrogen were added in the reactions, it would remain unchanged, and the yield of hydrogen chloride or of water would be just that corresponding to all of the chlorine or all of the oxygen.

In a considerable number of cases, however, especially at higher temperatures, there is after the reaction has ceased a considerable quantity of *both* of the reacting substances remaining. Thus in the reaction $CO + H_2O = CO_2 + H_2$, if one mol of carbon monoxide and one of steam are placed together at 1000°, the resulting mixture after all reaction has ceased (*i.e.*, at equilibrium) will be found to contain unchanged more than half of the water. If a mol of carbon dioxide and one of hydrogen are placed together, when equilibrium is reached the same relative quantities of the four substances will be found as when the reaction proceeded in the other direction; that is, somewhat more than half of the carbon dioxide and hydrogen will have reacted.

If we start with two mols of carbon monoxide and one of steam, a larger fraction of the steam will be reduced to hydrogen than when equal quantities were used, but the reaction does not proceed to the complete disappearance of any of the four substances no matter what relative quantities are employed. Similarly the use of four mols of carbon dioxide with one of hydrogen will

cause a much larger proportion of the hydrogen to form water. In general, an excess of any reacting substance increases the proportion of the substances formed from it, and decreases the proportion of the other substances reacting with the one in excess.

The laws of chemical equilibrium govern the relative quantities of substances present after equilibrium is attained, and are independent of the path by which this equilibrium was reached. Study of equilibrium will not, therefore, lead to definite conclusions as to the mechanism of the reaction. Thus, if one mol of carbon monoxide, one mol of hydrogen, and a half mol of oxygen are mixed and exploded, the law of chemical equilibrium will describe the condition of the system when equilibrium is reached and practically all of the oxygen is used up. But it will give no indication of whether oxygen combined with carbon monoxide to form carbon dioxide, which then reacted with hydrogen; or whether oxygen reacted with hydrogen to form water, which was then attacked by the carbon monoxide. It is immaterial which path was followed, so far as the *final* state of the system is concerned.

Relation among the Partial Pressures.—It has been found that the product of the partial pressures of carbon dioxide and hydrogen, divided by the product of the partial pressures of carbon monoxide and steam, is always the same at equilibrium for a given temperature, no matter what relative quantities of the substances were present at the start. This may be expressed by the equation

$$\frac{p_{CO_2} p_{H_2}}{p_{CO} p_{H_2O}} = \text{const.},$$

which is an expression of the *law of mass action*, or the law of chemical equilibrium. In words, this equation states that the product of the partial pressures of all the substances formed in a reaction, divided by the products of the partial pressures of all the substances reacting, is a constant for each reaction at a given temperature. The numerical value of the equilibrium constant changes considerably with temperature.

When more than one molecule of a substance is involved in the chemical equation of a reaction, the partial pressure of that substance in the equilibrium expression must be raised to the power which is its coefficient in the chemical equation. For

example, the equation for the dissociation of hydrogen molecules into atoms at very high temperatures is $H_2 = 2H$, and the equilibrium expression is, therefore,

$$\frac{p_{H}{}^2}{p_{H_2}} = K.$$

Similarly, in the reaction of the Deacon process for chlorine, $4HCl + O_2 = 2H_2O + 2Cl_2$, the equilibrium expression is

$$\frac{p_{H_2O}{}^2 p_{Cl_2}{}^2}{p_{HCl}{}^4 p_{O_2}} = K.$$

In reactions such as this one, it is important to know whether the water formed really exists as a vapor in the reacting mixture or whether, as a result of condensation, liquid water has been formed. In the latter case, the partial pressure of water would be only its vapor pressure at the temperature in question, regardless of the quantity which has been formed. The expression as written would contain this vapor pressure as the partial pressure of the water, and the equilibrium would be that corresponding to this pressure, not to the pressure calculated by assuming all of the water in the form of vapor.

In formulating mass-action expressions it has become customary to write the partial pressures or concentrations of the *products* of a reaction as shown by a chemical equation in the *numerator* of the equilibrium expression, and the pressures or concentrations of the reacting substances in the denominator. It will be evident that an incomplete reaction may be written in two ways, for example, $CO + H_2O = CO_2 + H_2$ or $CO_2 + H_2 = CO + H_2O$; and that, according to which way it is written, the pressures of carbon monoxide and water may appear in either the numerator or denominator. It is a matter of indifference which way the chemical equation is written, so long as the equilibrium expression is written to correspond to it. Later we shall have occasion to consider a relation between the equilibrium constant and the heat absorbed by a chemical reaction involved in it; and the sign of this heat absorption will also depend on which way the chemical reaction is written. All confusion will be avoided if the chemical reaction is always written down, the proper heat absorption, ΔH, is calculated to correspond to it as stated, and then the equilibrium expression is written in the way just out-

lined. The choice of units in which to express the partial pressures is a matter of convenience, but in employing a given value of an equilibrium constant it is essential that the unit used in calculating it be adhered to in further calculations. Partial pressures are usually expressed in atmospheres or less often in millimeters of mercury; when concentrations are used, these are always mols per liter. As temperature has a considerable effect upon equilibrium, it is essential to state at what temperature the equilibrium constant was obtained, and in experimental work it is necessary to maintain this constant temperature while equilibrium is being reached.

General Law of Chemical Equilibrium.—This law, often called also the law of mass action, may be stated as follows: At equilibrium the product of the partial pressures of the substances formed in a reaction, each raised to a power which is the coefficient of its formula in the chemical equation, divided by the product of the partial pressures of the reacting substances, each raised to a power which is the coefficient of its formula in the chemical equation, is a constant. Thus for the general reaction

$$aA + bB + \ldots = eE + fF + \ldots,$$

the condition of equilibrium at any specified temperature is

$$\frac{p_E^{\,e} p_F^{\,f} \ldots}{p_A^{\,a} p_B^{\,b} \ldots} = K_p. \qquad (1)$$

The equation may be derived[1] from the laws of thermodynamics for a system of ideal gases, or for solutes which conform to the simple laws of ideal solutions. In the latter case the equilibrium expression is written in terms of the molal concentrations of the substances involved, *i.e.*,

$$\frac{C_E^{\,e} C_F^{\,f} \ldots}{C_A^{\,a} C_B^{\,b} \ldots} = K_c. \qquad (2)$$

This law has been tested and confirmed experimentally, both for gaseous equilibrium and for equilibrium in solutions. Its deviations are usually not greater than those found between the measured and ideal properties of solutions or gases already considered. This law is perhaps the most important law of

[1] WASHBURN, *J. Am. Chem. Soc.*, **32**, 472 (1910); LEWIS, G. N., *Proc. Am. Acad. Arts Sci.*, **43**, 259 (1907).

physical chemistry; its proper application will show what procedure is necessary to increase the yield of a desired product in a chemical reaction, or what should be done to decrease the yield of an undesirable product. It indicates the precautions to be observed in analytical chemistry, and enables us to calculate in solutions the extent to which a reaction will take place, the fraction of a substance hydrolyzed, the concentration of one substance from that of another, the quantity of a reagent necessary to convert one solid completely into another, and many other similar quantities which are of importance.

We may illustrate the application of this law by considering the equilibrium constant for the reaction $H_2 = 2H$, for which the equilibrium constant may be calculated from Langmuir's experimental data.[1] At 3000° absolute and 1-atmosphere pressure hydrogen is 13 per cent dissociated. If we formulate the equilibrium upon a basis of 2.016 grams of hydrogen, each mol of H_2 which dissociates yields $2H_1$ or 0.26 mol of H_1, and 0.87 mol of H_2 remain; total mols 1.13. The partial pressure of H_1 is the product of its mol fraction and the total pressure, or $0.26/1.13 = 0.23$ and for H_2, 0.77 atmosphere, from which K is $(0.23)^2/0.77 = 0.0686$. Let us now calculate x, the fractional dissociation when the total pressure is 1 mm. or 0.00131 atmosphere. If x mols of H_2 dissociate, there are formed $2x$ mols of H_1, and $1 - x$ mols of H_2 remain. The total number of mols per formula weight is $1 + x$, the partial pressure of H_1 is $0.00131\ [2x/(1 + x)]$, and that of H_2 is $0.00131(1 - x)/(1 + x)$. Upon substituting these partial pressures in the equilibrium expression and solving for x we find 0.96, which means that at 3000° and 0.00131 atm. pressure hydrogen is 96 per cent dissociated into atoms. Experiment shows 94 per cent for these conditions.

It will be noted that at lower pressures the fraction dissociated is much greater; and this is to be expected from the equilibrium expression. If the total pressure were suddenly reduced to one-tenth of its value (so quickly that no reaction took place), each partial pressure would be reduced to one-tenth of its original value. But since the pressure of the atoms is squared while that of the molecules is to the first power, the value of p^2_H/p_{H_2} has been reduced below K, and the system is no longer in equi-

[1] LANGMUIR, *J. Am. Chem. Soc.*, **37**, 417 (1915).

librium. It will, therefore, react to restore equilibrium by increasing the pressure of the atoms at the expense of the molecules; that is, dissociation will proceed until the ratio of p^2_H/p_{H_2} returns to its proper value for the temperature in question.

This illustrates a general principle known as the law of Le Chatelier-Braun, which states that a system to which a change of pressure is applied will react in such a way as to relieve that change of pressure. Thus if the pressure is decreased and the system expands, it will react in the direction which corresponds to an expansion. In the case above this was seen to take place. Similarly, if the pressure on the system is increased, a part of the increased pressure will be relieved by a decrease in the number of gas particles (the single atoms act as molecules in their effect on the pressure), following the reaction $2H = H_2$.

Study of Gaseous Equilibrium.—(*a*) It has already been stated that the conditions of equilibrium change with the temperature. This fact makes the study of equilibrium somewhat difficult, since a sample cannot be cooled for analysis without changing its composition in case the reaction is a rapid one. It is, therefore, necessary in most cases to measure the partial pressures or concentrations of substances by some physical method which does not remove any substance from the equilibrium mixture. One method of simplifying the study of equilibrium has been mentioned above. If any substance taking part in a gaseous reaction is also present as a liquid, its partial pressure in the system is at all times the vapor pressure of the pure substance. When this is determined in advance, one of the partial pressures is fixed by the presence of the liquid. From the chemical equation it is usually possible to establish relations among the partial pressures, such that from a single determination of the density of an equilibrium mixture it is possible to calculate all of the partial pressures.

The reaction between water vapor and sulfur, forming hydrogen sulfide and sulfur dioxide according to the equation

$$2H_2O + 3S = 2H_2S + SO_2,$$

has been studied[1] in this simplified way, by employing an excess of sulfur in the reaction chamber. This chamber was immersed

[1] Lewis and Randall, *J. Am. Chem. Soc.*, **40**, 362 (1918).

in a bath of boiling sulfur at 450° as shown in Fig. 51. The pressure of sulfur vapor at its boiling point is equal to that of the atmospheric pressure upon it; and since the sulfur in the reaction bulb was also at this temperature, the partial pressure of sulfur was obtained by reading the barometer at the time of the experiment. The equilibrium expression is, therefore,

$$\frac{p^2_{H_2S} p_{SO_2}}{p^2_{H_2O}} = kp_S = K.$$

It is permissible to combine the value of k and the pressure of sulfur into a single constant K under these conditions, for in the

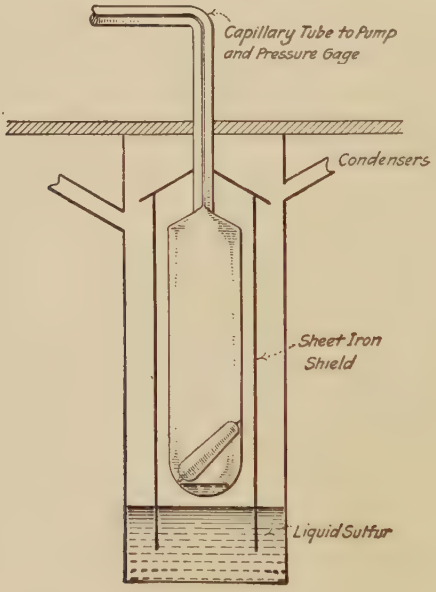


Fig. 51.

presence of excess sulfur its partial pressure in an equilibrium mixture is maintained constant at the vapor pressure of pure sulfur.

A weighed bulb of water and an excess of sulfur were introduced into the reaction vessel, and all of the air was pumped out. This was then sealed to a manometer tube, from which the total pressure could be determined, and suspended in a bath of boiling sulfur to maintain it at a constant temperature. The water was weighed in a very thin glass tube completely filled

with liquid and sealed shut. When this was heated, expansion of the water burst the bulb and started the chemical reaction. Consider the water and sulfur at 450° before any reaction has taken place. The partial pressure of the water may be calculated from the simple gas law $pv = (m/18)RT$, from the weight of water employed, and from the volume of the reaction chamber. The chemical reaction is $2H_2O + 3S = 2H_2S + SO_2$, according to which a mol of hydrogen sulfide is formed for every mol of water reacting. The sum of the mols of water and hydrogen sulfide remains constant and, therefore, the sum of their partial pressures is at all times equal to the original pressure of the water vapor before the reaction occurred. In the presence of liquid sulfur, the partial pressure of sulfur remains constant, for more sulfur vaporizes as the reaction proceeds. Any *increase* in pressure must, therefore, be due to the formation of sulfur dioxide.

TABLE 84.—EQUILIBRIUM IN THE REACTION BETWEEN SULFUR AND WATER
(The partial pressures are shown in millimeters of mercury)

Grams water	Volume cubic centimeters	Pressure calculated for no reaction	Observed equilibrium pressure	p_{SO_2}	p_{H_2S}	p_{H_2O}	p_S	$K_p = \frac{p^2_{H_2S}\, p_{SO_2}}{p^2_{H_2O}}$
0.0441	151	1,501	1,554	53	106	624	771	1.52
0.0549	204	1,435	1,476	41	82	592	761	0.80
0.0470	167	1,471	1,519	48	96	609	766	1.19
0.0540	117	1,913	1,978	65	130	1,019	764	1.06
						Average	....	1.17

Let us consider in detail the third experiment in Table 84, where the weight of water was 0.047 gram. The volume of the reaction chamber, after allowing for the space occupied by liquid sulfur, was 167 c.c.; the pressure of water vapor (in millimeters) before any reaction has taken place is calculated from the equation $\frac{p}{760} \times 167 = \frac{0.0470}{18} \times 82 \times (273 + 450)$, whence $p = 705$ mm. The barometric pressure was 766 mm., and this is, therefore, the sulfur pressure in the bulb. Then the total pressure before any reaction took place was 705 + 766 = 1471; and the measured equilibrium pressure was 1519 mm. As shown by the chemical equation, if the pressure of sulfur is kept constant, any *increase* in pressure must be due to the formation of sulfur dioxide, since the sum of the partial pressures of water and hydrogen sulfide remains unchanged. Then 1519 − 1471 = 48 is p_{SO_2}. The chemical equation further shows that there are two molecules of hydrogen sulfide formed for every molecule of sulfur dioxide, hence the partial pressure of hydrogen sulfide must be $2p_{SO_2}$ or 96 mm. But $96 + p_{H_2O} = 705$, or $p_{H_2O} = 609$. The equilibrium constant is, therefore, $(96)^2(48)/(609)^2 = 1.19$. It is usual in equilibria of this kind to include the partial pressure of the substance present as a liquid or solid in the value of the

equilibrium constant. Thus the constant 1.19 is really $k \times p_s$, but since each of these is constant, the calculation is simplified to this extent. For cases in which the sulfur pressure is not kept constant by the presence of an excess of its liquid, this equilibrium constant does not, of course, apply; but an expression containing the partial pressure of sulfur would apply.

Concordance among the constants obtained is not all that could be desired, but the difficulties in making measurements are very great. An error of one-half of 1 per cent in the total pressure is 7 mm., but since the small partial pressure of sulfur dioxide is obtained by subtracting the calculated total pressure from the observed total pressure, this 7-mm. error will appear as 7 mm. on the total of only 48-mm. pressure of sulfur dioxide, or an error of 15 per cent. The experimental error is thus increased 30 fold.

Similar considerations apply in case one of the reacting substances is also present as a solid phase, for at every temperature the sublimation pressure of a solid is a characteristic property of it, unchanged by the presence of other gases. A determination of this sublimation pressure in a separate experiment establishes its partial pressure in the equilibrium mixture for the temperature in question.

(*b*) In reactions involving hydrogen at high temperatures, advantage may be taken of the fact that platinum is permeable to this gas and not to other gases. Thus a platinum tube inserted into a reaction chamber allows free penetration of hydrogen, and its partial pressure is measured by a manometer attached to the platinum tube. This method has been applied to the equilibrium

$$CO_2 + H_2 = CO + H_2O$$

at high temperatures.[1] A gaseous mixture containing known proportions of carbon dioxide and hydrogen was brought to equilibrium at a total pressure of 1 atmosphere. As the total number of mols of gas does not change during the chemical reaction, no change of pressure is observed. But a decrease in hydrogen pressure can take place only when water is formed from it; hence the difference between the starting pressure of hydrogen (calculated from its mol fraction in the original mixture) and the equilibrium pressure represents water-vapor pressure. From the chemical reaction it follows that there is a mol of carbon monoxide formed for each mol of hydrogen used, *i.e.*, for each mol of water formed. And there is a mol of carbon dioxide used up for every mol of carbon monoxide formed. Thus a measure-

[1] HAHN, *Z. physik. Chem.*, **44**, 513 (1903).

ment of hydrogen pressure gives (*a*) the partial pressure of hydrogen, (*b*) the partial pressure of carbon monoxide, (*c*) the partial pressure of water vapor (each of these last two being equal to the decrease in hydrogen pressure during reaction), and by difference (*d*) the pressure of carbon dioxide. Table 85 shows the results of experiments at 986°, together with values of the constant

$$\frac{p_{CO}p_{H_2O}}{p_{H_2}p_{CO_2}} = K_p.$$

TABLE 85.—EQUILIBRIUM AT 986°

Original mixture		Equilibrium mixture			
Per cent CO_2	Per cent H_2	Per cent CO_2	Per cent $CO = H_2O$	Per cent H_2	K_p
10.1	89.9	0.69	9.4	80.5	1.60
30.1	69.9	7.15	22.96	46.93	1.58
49.1	51.9	21.22	27.90	22.95	1.60
60.9	39.1	34.43	26.45	12.67	1.60
70.3	29.7	47.50	22.82	6.85	1.60
			Average	.....	1.596

An interesting feature of this equilibrium is the calculation of dissociation constants from it. So far nothing has been said about the presence of oxygen in this mixture, and there is, in fact, only an insignificant quantity present. Its partial pressure would have no effect upon the total pressure which could be detected by experimental means. But the small quantity of it present must satisfy the dissociation equilibria $2H_2O = 2H_2 + O_2$ and $2CO_2 = 2CO + O_2$, for which the equations are

$$\frac{p^2_{H_2}p_{O_2}}{p^2_{H_2O}} = K_{H_2O} \text{ and } \frac{p^2_{CO}\,p_{O_2}}{p^2_{CO_2}} = K_{CO_2}.$$

Upon dividing the second of these dissociation expressions by the first, and extracting the square root, we obtain

$$\frac{p_{CO}p_{H_2O}}{p_{H_2}p_{CO_2}} = \sqrt{\frac{K_{CO_2}}{K_{H_2O}}} = K,$$

which is the equilibrium expression given above for the reaction $CO_2 + H_2 = CO + H_2O$. This furnishes a means of calculating

equilibrium constants from dissociation constants, or of calculating dissociation constants from measurements of equilibria such as this one.

(*c*) Other methods are applicable to certain types of equilibrium; thus a determination of the density of an equilibrium mixture establishes the mol fraction of each constituent in the dissociation of phosphorus pentachloride. Let x be the fractional dissociation into phosphorus trichloride and chlorine, and let D be the weight of a liter of equilibrium mixture at the temperature T. Then for each formula weight of pentachloride put into the mixture, x mols of chlorine and x mols of trichloride form, and $(1 - x)$ mols of pentachloride remain. The mol fraction of chlorine is, therefore, $x/(1 + x)$, since $1 + x$ is the total number of mols present per formula weight of pentachloride; this is also the mol fraction of trichloride, and $(1 - x)/(1 + x)$ is the mol fraction of pentachloride. At a temperature T the volume of a mol of mixture is RT/p liters, where p is the total pressure in atmospheres, and R is 0.082. If D is the weight of a liter, a mol of mixture weighs DRT/p grams. The molecular weights of chlorine, trichloride, and pentachloride being, respectively, 71, 137.4, and 208.3, and the number of mols of each in a mol of mixture being the mol fraction of each, we have

$$\frac{x}{1+x}71 + \frac{x}{1+x}137.4 + \frac{1-x}{1+x}208.3 = \frac{DRT}{p},$$

from which the fractional dissociation may be calculated.

(*d*) In other cases one of the reacting substances may have a characteristic color which varies with its concentration; this may then be determined by comparison with color standards containing that substance alone in known quantity. Other methods must often be devised to fit the problem in hand, but these may serve as illustrations of typical methods for studying gaseous equilibrium.

Equilibrium in solution may sometimes be studied by the conductance of a solution as a whole (which varies with the concentrations of ionized solutes, but takes no account of non-ionized substances); from determinations of the vapor pressure of some constituent which is volatile; from distribution of a solute between the phase under examination and a second phase in which only one reacting substance is soluble; from freezing-

of hydrochloric acid it is ionized about 3 per cent as shown by the ratio Λ/Λ_0.

Similar considerations would apply to any weak acid in the presence of a strong acid, to any weak base in the presence of a strong base, and to a weak acid or a weak base in the presence of its salts. For example, if 0.1 formal ammonium hydroxide is mixed with an equal volume of 0.1 formal ammonium chloride solution, the base in the resulting solution is about 0.04 per cent ionized. This probably explains why the relatively insoluble hydroxides of magnesium and ferrous iron are not precipitated by ammonium hydroxide in the presence of ammonium salts. Such exceedingly insoluble hydroxides as ferric hydroxide or aluminum hydroxide are precipitated even in the presence of ammonium salts, for the hydroxide ion concentration required is very small, and is reached even in the presence of large concentrations of ammonium ions.

TABLE 87.—IONIZATION CONSTANTS AT 25°

Formic acid	214×10^{-5}	Carbonic acid K_1	3.5×10^{-7}
Acetic acid	18×10^{-6}	K_2	5.4×10^{-11}
Propionic acid	14.5×10^{-6}	Ammonia	18×10^{-6}
Acetoacetic acid	150×10^{-6}	Pyridine	23×10^{-10}
Chloroacetic acid	$1{,}550 \times 10^{-6}$	Aniline	4×10^{-10}
Benzoic acid	60×10^{-6}	Hydrocyanic acid	7×10^{-10}
Nitrous acid	450×10^{-6}	Boric acid	6.6×10^{-10}
Hydrofluoric acid	$7{,}000 \times 10^{-6}$	Phenol	1.1×10^{-10}
Phosphoric acid K_1	10^{-2}		
K_2	2×10^{-7}		
K_3	3.6×10^{-13}		

Partly from KENDALL, *J. Am. Chem. Soc.*, **38,** 1480(1916); **39,** 2317(1917); LUNDEN, *J. chim. phys.*, **5,** 574 (1907); BOYD, *J. Chem. Soc. London*, **107,** 1538 (1915); LEWIS and RANDALL, *J. Am. Chem. Soc.*, **37,** 458 (1915).

Highly Ionized Substances.—When the conductance ratio is employed to calculate the "ionization constants" for highly ionized acids, bases, and salts in aqueous solutions, as we have done above, there is found no constant value. In other words, the law of mass action does not apply to the ionization of a salt. Up to the present, no satisfactory explanation for this anomaly has been found. The mass-action law applies to cases not involv-

ing ionized substances so well that it is natural to inquire where the theory of ionization is at fault. But the ionization theory has been useful in explaining abnormally large freezing-point depressions, in showing why all acids are sour, why all chlorides precipitate silver chloride when silver nitrate is added, why all copper salts are blue when dissolved in water, and in explaining the mechanism of electrolytic conduction; so that one is not ready to discard it. At present there exists only a sort of compromise, accepted for lack of a better explanation, but recognized as highly unsatisfactory.

The law of mass action may not be expected to hold rigorously except for ideal solutes, but the deviations to be expected from it are ordinarily not more than those between other observed and calculated properties of solutions. One is quite unprepared for such wide discrepancies as those shown[1] by the ionization "constants" of Table 88. The equilibrium "constant" is not even roughly constant, but increases a hundred fold for potassium chloride and a million fold for potassium ferrocyanide.

TABLE 88.—"IONIZATION CONSTANTS" FOR SALTS OF DIFFERENT TYPES

KCl		$Ba(NO_3)_2$		$K_4Fe(CN)_6$	
Concentration	K	Concentration	K	Concentration	K
0.0001	0.0075	0.001	0.000017	0.0005	0.7
0.001	0.035	0.005	0.00018	0.0020	18.0
0.01	0.132	0.01	0.00045	0.012	1,171.
0.1	0.495	0.10	0.97	0.1	41,190.
1.0	2.22	.....	.....	0.4	842,100.

Since the law of chemical equilibrium may be derived from thermodynamics for ideal solutes, it is clear that some or all of the molecular species involved in the equilibrium between a dissolved salt and its ions are very far from ideal solutes. The law of mass action holds in solutions where no ions are involved; it would be natural in view of this to state that the ions are not "normal" solutes, and ascribe all of the abnormal behavior to

[1] LEWIS, *Z. physik. Chem.*, **70**, 215 (1909). Printed in English.

them on account of their electric charges. But ions appear to obey the laws of ideal solutes in very dilute solutions to a fairly close approximation.

It has already been suggested that there is no satisfactory way of measuring the extent of ionization. An assumption of complete ionization does not appear to help us out of the difficulty, for even in dilute solutions the measured activity of an ion is considerably less than concentration of the salt. Even if salts and "strong" acids and bases are completely ionized, "weak" electrolytes are certainly not completely ionized, and we are confronted with the difficulty of separating electrolytes into these two classes. The law of mass action may be made to hold rigorously only by employing activities. It should be remembered in this connection that activities are *defined* as mass-action effects, so that in this case the law holds *by definition*.

Empirical Ionization Equations.—Many attempts have been made to retain the conductance ratio $\Lambda/\Lambda_0 = \alpha$ as a measure of the "fractional ionization" and to find some law which governs the change in this ionization with concentration for salts and other highly ionized solutes. Most of these attempts involve some empirical alteration in the law of chemical equilibrium which has no theoretical basis, and whose only purpose is to bring the change of $\Lambda/\Lambda_0 = \alpha$ with the concentration into agreement with experiments. The modification proposed by Storch is

$$\frac{(C\alpha)^n}{(1-\alpha)C} = K \tag{4}$$

and it has been found by trial that the value of n necessary to make this equation fit experimental results is between 1.40 and 1.55 for all types of salts, and over a wide range of temperature.[1] If the value of n is taken as 1.5, the equation becomes the Rudolphi formula. While this equation expresses the change of conductance ratio quite well for moderate concentrations, it does not reduce to the law of mass action for very low salt concentrations where this law is valid for electrolytes.[2]

[1] NOYES, *Science*, **20**, 584 (1904); *J. Am. Chem. Soc.*, **30**, 335 (1908); SHERRILL, *J. Am. Chem. Soc.*, **32**, 741 (1910).

[2] WASHBURN, *J. Am. Chem. Soc.*, **40**, 145 (1918).

To adapt this equation and the law of mass action to their respective concentration ranges, Kraus and Bray[1] combined the equation of Storch with the mass-action law into the form

$$\frac{(C\alpha)^2}{C(1-\alpha)} = K + D(C\alpha)^m, \tag{5}$$

in which K is the mass-action constant, D and m are constants for each substance studied, and C and α have their former significance. When the concentration is small, the term containing D becomes small in comparison to K, and the equation assumes the form of the familiar mass-action law. When the concentration is large, K is small compared to the D term, and the equation becomes that of Storch. A test of this equation for all of the available data in solvents other than water as well as in aqueous solutions shows that it describes the change of conductance with concentration. The disadvantage of the equation is that the constants K, D, and m must be determined for each substance in each solvent by at least three measurements of conductance at different concentrations. The simpler equations to which it reduces at high and at low concentrations will on that account be found much more useful. In considering a salt for which the value of n in the Storch equation is not known, satisfactory calculations can be made by taking $n = 1.5$.

Polybasic Acids.—Weak dibasic acids, such as phosphoric acid, carbonic acid, tartaric acid, and hydrogen sulfide, ionize in steps, and a mass-action expression may be written for each step. For example, carbonic acid gives in its first-step ionization hydrogen ions and bicarbonate ions, H^+ and HCO_3^-, and the corresponding mass-action expression is

$$\frac{(H^+)(HCO_3^-)}{(H_2CO_3)} = 3.5 \times 10^{-7} = K_1.$$

The bicarbonate ion itself acts as a weaker acid than carbonic acid from which it came, and ionizes into hydrogen ions and carbonate ions, $HCO_3^- = H^+ + CO_3^{--}$.

$$\frac{(H^+)(CO_3^{--})}{(HCO_3^-)} = 5.4 \times 10^{-11} = K_2.$$

[1] *J. Am. Chem. Soc.*, **35**, 1315–1434 (1913).

It should be noted that K_2 is written for the *ionization of an ion* into other ions. The expression (H^+) in the numerator of K_2 indicates total hydrogen ion concentration in solution, not merely that part of it which came from the ionization of bicarbonate ions. From the very small ionization constant K_2 it is seen that only an exceedingly small concentration of carbonate ions ever exists in the presence of a moderate hydrogen ion concentration. This probably explains the ready solubility of carbonates in acid, since their carbonate ions are immediately converted into bicarbonate ions as soon as they pass into solution. From these constants the ratio of the carbonate ion concentration to the bicarbonate ion concentration, for example, can be calculated when the hydrogen ion concentration is known.

The first-step ionization of phosphoric acid does not conform very closely to the law of mass action, but the second and third steps correspond to the ionization of very weak acids,[1] and do conform to this law. The chemical equations are $H_2PO_4^- = H^+ + HPO_4^{--}$ and $HPO_4^{--} = H^+ + PO_4^{---}$; the mass-action equations are

$$\frac{(H^+)\,(HPO_4^{--})}{(H_2PO_4^-)} = 2 \times 10^{-7} = K_2;$$

and

$$\frac{(H^+)(PO_4^{---})}{(HPO_4^{--})} = 3.6 \times 10^{-13} = K_3.$$

Equilibria Involving Ions.—There are many chemical reactions which appear to take place between ions, and whose equilibrium conditions depend only upon the ion concentrations involved. In this book, in formulating equilibrium expressions for these reactions, we shall leave out of consideration the concentrations of non-ionized molecules of strong electrolytes, and consider the ions as solutes which conform approximately to the mass-action law. While this procedure is not a very satisfactory one, it leads to approximate agreement with the experimentally determined values. In these expressions the molecules of weak electrolytes are considered, since they conform to the mass-action law. For example, the reaction between a

[1] Abbott and Bray, *J. Am. Chem. Soc.*, **31**, 729 (1909).

salt of a weak acid like acetic acid and another acid such as nitrous acid would be

$$NaAc + HNO_2 = NaNO_2 + HAc,$$

the equilibrium expression for which is written

$$\frac{(HAc)(Na^+)(NO_2^-)}{(Na^+)(Ac^-)(HNO_2)} = K.$$

The equilibrium expression for the hydrolysis of ammonium acetate, $NH_4Ac + H_2O = NH_4OH + HAc$, is written

$$\frac{(NH_4OH)(HAc)}{(NH_4^+)(Ac^-)} = K.$$

When the equilibria are so formulated, a value of K is obtained from experiments which enables us to calculate approximately the concentrations at equilibrium in another system involving the same substances. The concentration (more properly, the activity) of water in a solution which is dilute does not change as the reaction progresses, and this concentration is understood to be included in the value of K for the hydrolysis. In the presence of ammonium acetate, the fractional ionization of acetic acid is negligibly small, for the high concentration of acetate ions necessitates a very small concentration of hydrogen ions. Ammonium hydroxide in the presence of an ammonium salt is not appreciably ionized. Similarly, in the reaction above, nitrous acid does not ionize to an appreciable extent in the presence of sodium nitrite and acetic acid does not ionize in the presence of sodium acetate. These acids can, therefore, be treated as if substantially all of each one present were in the non-ionized state.

In formulating mass-action expressions in the way just explained we have used salt concentrations for ion activities. For example, in the mass-action formulation for equilibrium between sodium acetate and nitrous acid, the nitrite ion activity $C\gamma$ should have been used in place of the concentration of sodium nitrite. There is at present no simple method known for calculating the activity coefficient of an ion in a salt mixture and we omit γ only because we do not know how to calculate it. However, if it be assumed (without much ground for having made the assumption) that the activity coefficient for nitrite ion is the same

as that for acetate ion, an equilibrium expression would have been formulated from which γ would cancel out. Thus the fact that equation (6) above leads to results in agreement with experiment is not evidence of complete dissociation in solution, but rather an indication that the activity coefficients for the two ions are not greatly different in the equilibrium mixture.

The Ionization of Water.—Measurements of the conductance of pure water, made primarily to determine the correction to be applied in calculating the conductance of dilute solutions, have led to the conclusion that the concentration of hydrogen ion in it is 10^{-7} formal, or one equivalent of hydrogen ion in ten million liters of water; the concentration of hydroxide ion, OH^-, in pure water is also 10^{-7}. These ions result from the ionization of water itself, $H_2O = H^+ + OH^-$, not from the presence of impurities in it. Considerations such as we are about to take up have shown that the product of these ion concentrations is a constant in all water solutions for a given temperature. Thus the product $(H^+)(OH^-) = 10^{-14} = K_w$ is constant for a temperature of 25°, whatever the other substances present. This means that in a solution of a base where the concentration of hydroxide ions is quite high, the hydrogen ion concentration is correspondingly reduced, and in a solution of an acid the hydroxide ion concentration is correspondingly reduced. As is the case with most equilibria, this ion product changes with the temperature. It will be noticed that, in spite of the fact that water is an extremely weak electrolyte (*i.e.*, a very slightly ionized one), we have not included the non-ionized portion of it in the equilibrium expression. This might have been written $(H^+)(OH^-) = K'(H_2O) = K_w$, where the term K_w is understood to include activity of the water molecules. There is a difficulty in considering the concentration of a solvent when it is thought of as a dissolved substance at the same time; but to avoid this, it is only necessary to notice that the mol fraction of water in a dilute solution is practically constant at all times, and that, therefore, its mass-action effect is constant. The product of this mass-action effect and the constant K' above is K_w, called the ionization constant of water. Its value for several temperatures is shown in Table 89.

TABLE 89.—IONIZATION CONSTANT OF WATER AT VARIOUS TEMPERATURES

Temperature	Values of $K_w \times 10^{14}$ as determined by				
	Noyes[1] Kanolt[6]	Lunden[2]	Lorenz and Bohi[3]	Heydweiller[4]	Kohlrausch[5]
0°	0.089	.....	0.136	0.116	
18°	0.46	0.31 (10°)	0.716	0.59	0.78
25°	0.82	1.05	1.216	1.04	1.05
50°	4.5	5.17	8.75	5.66	
75°	16.9	....	28		
100°	48	....	73	58.2	

[1] *Carnegie Inst. Pub.*, **63**, 346 (1907); *J. Am. Chem. Soc.*, **32**, 159 (1910).
[2] *J. chim. phys.*, **5**, 574 (1907). Hydrolysis of ammonium borate.
[3] *Z. physik. Chem.*, **66**, 733 (1909). E.m.f. of acid-alkali cell.
[4] *Ann. Physik* (4), **28**, 503 (1909). Heat of neutralization.
[5] *Wied. Annalen*, **53**, 209 (1894). Conductivity of pure water.
[6] *J. Am. Chem. Soc.*, **29**, 1402 (1907). Hydrolysis of ammonium salts.

Hydrolysis.—When a salt like potassium cyanide is dissolved in water, the cyanide ions from it find themselves in the presence of a small concentration of hydrogen ions from the ionization of water. Hydrocyanic acid is only very slightly ionized and the concentration of cyanide ions is quite high; there is a marked tendency of the ions of the acid to combine into electrically neutral molecules, and this takes place. This leaves potassium ions and hydroxide ions together, but these ions appear to have little tendency to combine. To make up the loss in hydrogen ions in the formation of hydrogen cyanide, more water molecules ionize, and the chemical reaction

$$KCN + H_2O = KOH + HCN$$

proceeds until equilibrium is established. This reaction is called hydrolysis; it will be seen that it is the reverse of neutralization. Potassium cyanide is about 1.2 per cent hydrolyzed in 0.1 formal solution at 25°, about 3.5 per cent hydrolyzed at 0.01 formal, and about 12 per cent hydrolyzed at 0.001 formal. Following the convention adopted above (of writing equilibrium expressions in terms of the ions of largely ionized substances), and leaving out of the formulation the concentration of the water, since it is

essentially unchanged by the small quantity of it reacting, we have

$$\frac{(K^+)\,(OH^-)\,(HCN)}{(K^+)(CN^-)} = K_h$$

as the equilibrium expression for the reaction. The concentration of potassium ion may be canceled from the expression, and if we multiply both numerator and denominator by the concentration of hydrogen ion, we have

$$\frac{(H^+)\,(OH^-)\,(HCN)}{(H^+)(CN^-)} = K_h.$$

It will be seen that this expression is the quotient of the expression $(H^+)(OH^-) = K_w$ divided by the ionization expression for hydrocyanic acid, $(H^+)(CN^-)/(HCN) = K_a$, and since each of these values is known, we have at once a method of evaluating the equilibrium constant without recourse to separate measurements of this particular equilibrium. Canceling out now the hydrogen ion concentration (which was inserted merely to make clear the method of evaluating the constant), we have

$$\frac{(OH^-)(HCN)}{(CN^-)} = K_h = \frac{K_w}{K_a}. \qquad (6)$$

Now denoting by C the formal concentration of potassium cyanide and by h the fraction of the salt which has undergone hydrolysis, the concentration of hydrocyanic acid is hC, the concentration of potassium hydroxide is also hC, and the concentration of the remaining potassium cyanide is $(1 - h)C$. Substituting in the above expression for equilibrium, we have as the general equation for this type of hydrolysis

$$\frac{hC \cdot hC}{(1 - h)C} = \frac{K_w}{K_a} = K_h. \qquad (6a)$$

When the salt of a strong acid and a weak base hydrolyzes, the expression for its fraction hydrolyzed may be derived in a manner exactly similar to that for the case of potassium cyanide just considered, and, putting K_b for the ionization constant of the weak base, the resulting equation may be written

$$\frac{hC \cdot hC}{(1 - h)C} = \frac{K_w}{K_b} = K_h. \qquad (7)$$

There remains to be considered the case where both the acid and base of a salt are weak electrolytes. Here there is a tendency for the positive ions of the salt to combine with the hydroxide ions of water, added to a tendency of the negative ions of the salt to combine with hydrogen ions from water. When both ions are thus removed, the hydrolysis will proceed much farther. We may write the chemical equation, taking ammonium acetate as an example,

$$NH_4Ac + H_2O = NH_4OH + HAc$$

and the equilibrium expression is

$$\frac{(NH_4OH)\,(HAc)}{(NH_4^+)(Ac^-)} = K_h. \tag{8a}$$

It is permissible here, as in the case before, to neglect the ionization of ammonium hydroxide and of acetic acid in the presence of ammonium acetate, since the highly ionized salt would repress the slight ionization of the weak acid and base. In order to see the method of evaluating this constant from the ionization constants involved, multiply both numerator and denominator by the product $(H^+)(OH^-)$, and on rearranging we have

$$\frac{(NH_4OH)\,(H^+)(OH^-)\,(HAc)}{(NH_4^+)(OH^-)\,(H^+)(Ac^-)} = \frac{K_w}{K_aK_b} = K_h.$$

Denoting as before the salt concentration by C and the fraction hydrolyzed by h (and dropping out the ion product of water in both numerator and denominator, since this was introduced only to make clear the method of evaluating the constant K_h), we may substitute for (NH_4OH) its equivalent hC, for (HAc) its equivalent hC (the chemical equation shows that acid and base are formed in equal quantities), and for the ion concentrations $(1 - h)C$, and we obtain the expression

$$\frac{hC \quad hC}{(1 - h)C \cdot (1 - h)C} = \frac{K_w}{K_aK_b} = \frac{h^2}{(1 - h)^2}. \tag{8}$$

This equation shows that the fraction hydrolyzed is independent of the concentration of the salt when both acid and base are slightly ionized. This is not the case for salts of a strong base or of a strong acid. Equation (8) shows further that the fractional hydrolysis increases as the ionization constant of the acid or base involved becomes smaller. For example, ammonium

acetate is about 0.5 per cent hydrolyzed at 25°, but ammonium borate and ammonium cyanide are about 40 per cent hydrolyzed.

The fourth possible case is that of a salt of a strong base and a strong acid, but in this case no hydrolysis takes place. It will be noticed that hydrolysis is the reverse of the process of neutralization; and since this latter is known to take place completely for equivalent quantities of a strong acid and a strong base, it is clear that the reverse process does not take place at all. Similarly, since salts of weak acids and weak bases are hydrolyzed, the reverse process of neutralization does not take place completely when equivalent quantities of acid and base are brought together, since it is a necessary condition of chemical equilibrium that the concentration ratios at equilibrium are independent of the direction from which equilibrium was approached.

It should be noted that the hydrolysis equations (6) and (8) apply only when there is no excess acid or base present; that is, they apply only to the hydrolysis of a salt when nothing is done to diminish hydrolysis. The more general equations (6*a*) and (8*a*) apply under *all* conditions, and show the way hydrolysis of a salt may be diminished by adding one of the products of hydrolysis. Caution should be observed in the use of the simpler equations (6) and (8) that they are used only under the conditions to which they specifically apply.

Distribution of a Base between Two Slightly Ionized Acids.—This distribution results when a mixture of acids is treated with a quantity of base insufficient to neutralize both of them. As stated at the beginning of the chapter, it is immaterial whether we consider that the base reacts with one of the acids, and the salt is reacted upon by the other acid, or whether a straight distribution results from partial neutralization of each acid. The chemical equation may be written for some simple method of attaining equilibrium, and the equilibrium expression formulated in accordance with this equation, without regard to the actual path by which equilibrium was attained. Suppose a liter of 0.2 formal potassium nitrite is mixed with a liter of 0.2 formal acetic acid; the reaction is $KNO_2 + HAc = HNO_2 + KAc$, for which the equilibrium expression is

$$\frac{(HNO_2)\,(K^+)\,(Ac^-)}{(HAc)\,(K^+)\,(NO_2^-)} = K.$$

The potassium ion concentration which appears in both numera tor and denominator of this expression may be canceled from it Neither of the weak acids will be ionized to an appreciabl extent in the presence of the highly ionized salts. Let x be th fraction of acetic acid which reacts according to the equation Since we have 0.2 mol of salt and 0.2 mol of acid in 2 liters, th total salt concentration is 0.1 mol per liter, and the free aci concentration is 0.1 mol per liter. The quantity of potassiun acetate formed is $0.2x$; hence its concentration is $0.1x$. Sinc nitrous acid is formed in equivalent amount according to th equation, its concentration is also $0.1x$. Similarly, the concen trations of potassium nitrite and acetic acid are each $0.1(1 - x)$ Substituting these quantities in the equilibrium expression, w have

$$\frac{(0.1x)(0.1x)}{0.1(1 - x)[0.1(1 - x)]} = K = \frac{x^2}{(1 - x)^2}.$$

This latter form of the mass-action expression applies only whe the acid and salt are present in equivalent quantity, since onl then will the concentrations cancel out of the equation; but th expression

$$\frac{(HNO_2)(Ac^-)}{(HAc)(NO_2^-)} = K$$

as first formulated for this chemical reaction applies regardles of the relative quantities of salt and acid first mixed. As means of obtaining the numerical value of K for this type equilibrium, it should be noted that the same expression ma be obtained by dividing the ionization expression for acetic aci by that for nitrous acid (canceling the hydrogen ion concentra tions, which must be the same when the two acids are presen in the same solution), and that the equilibrium may therefo be written

$$\frac{x^2}{(1 - x)^2} = K = \frac{K_{HAc}}{K_{HNO_2}}. \qquad (9$$

In a solution containing one equivalent of base to one equivalen of each of two acids, the quantities of the two acids combine with the base are to each other as the square roots of their ioniz tion constants, *i.e.*,

$$\frac{x}{1 - x} = \sqrt{\frac{K_{HAc}}{K_{HNO_2}}}.$$

A similar calculation can, of course, be made for the distribution of an acid between two bases; the chemical equation should first be formulated, then the equilibrium expression, and finally all of the concentrations should be expressed in terms of a single unknown quantity, such as the fraction of acid combined with one base.

When the acid and the salt reacting with it are not present at the same concentration, the equilibrium may be formulated as follows: Let C_a be the total acid concentration and C_s the total salt concentration in the mixture, and let the reaction be $KA + HA' = HA + KA'$, for which the equilibrium expression is

$$\frac{(HA)(A'^-)}{(HA')(A^-)} = K = \frac{K_{HA'}}{K_{HA}}.$$

As before, we may consider that the ionization of each weak acid in the presence of its salt is negligible. If y is the fraction of HA′ which has reacted with KA, yC_a is the concentration of HA, and also of KA′, which is formed in equal amount as shown by the equation. The concentration of unchanged HA′ is $C_a(1 - y)$, and the concentration of unchanged salt KA is $(C_s - yC_a)$. Substituting in the expression above,

$$\frac{(yC_a)(yC_a)}{C_a(1 - y)[(C_s - yC_a)]} = K = \frac{y^2C_a}{(1 - y)(C_s - yC_a)}. \quad (10)$$

It will be seen that when the acid concentration and the salt concentration are equal, this equation reduces to the simpler one first derived.

By means of these relations, the ionization constant of one acid may be determined from the ionization constant of another acid, provided there is a ready method of determining the equilibrium conditions. Such a method is not always easy, however, as it must be one which determines the concentration of some one substance (from which the concentrations of the others may be computed) without disturbing the equilibrium. Thus a titration of the solution will show only the total acid and give no indication of how much of each acid is present; the precipitation of an insoluble salt of one of the acids would remove both the acid and the salt without giving any indication of the proportion of each. If one of the acids formed is volatile, a determination of its pressure above the solution fixes its concentration in

the solution; if one of them is only slightly soluble, its concentration may be kept constant by keeping the solution saturated with it during the experiment. A sample of the equilibrium mixture may then be titrated for total acid, the amount of the slightly soluble one present at equilibrium is known from previous determinations of its solubility, and the concentration of the other acid may be obtained by difference. If one of the acids is soluble in benzene and the other acid is not, the first acid concentration in the equilibrium mixture may be determined by distribution experiments, in the way explained on page 136.

Indicators.—By reference to the equation showing the distribution of a base between two acids present in equivalent quantity (equation (9)), it will be seen that when one of the acids is much stronger than the other (*i.e.*, has a much larger ionization constant), the stronger acid is largely neutralized when the weaker acid is still largely uncombined. Let us calculate, as an example, the fraction of hydrocyanic acid freed from potassium cyanide by the addition of an equivalent quantity of acetic acid, which is a much stronger acid. If c is the total salt concentration and x is the fraction of hydrocyanic acid liberated by acetic acid, according to the chemical reaction

$$KCN + HAc = KAc + HCN,$$

the equilibrium expression corresponding to this reaction is

$$\frac{(Ac^-)(HCN)}{(CN^-)(HAc)} = \frac{cx \cdot cx}{c(1-x)\,c(1-x)} = \frac{K_{HAc}}{K_{HCN}} = K,$$

or

$$\frac{x}{1-x} = \sqrt{\frac{K_{HAc}}{K_{HCN}}} = \sqrt{\frac{18 \times 10^{-6}}{7 \times 10^{-10}}} = 160,$$

whence x is 0.994. Since this is the same equilibrium state as that obtained by adding a mol of potassium hydroxide to a solution containing a mol of free acetic acid and one of free hydrocyanic acid, it will be seen that practically all of the acetic acid is neutralized, and only a small fraction of hydrocyanic acid reacts.

Now suppose hydrocyanic acid to be replaced by some other acid which is as weak, but which changes color upon being neutralized. When one mol of base has been added, practically all of the acetic acid is neutralized, and only a very small portion

of the other acid. Addition of more base causes the weaker acid to react, with an accompanying color change. Thus the weaker acid may be made to serve as an indicator for titrating the stronger acid.

Further study of the distribution of a base between two acids shows that when one acid is at a higher concentration than the other, a greater fraction of the one present in excess is neutralized than when both acids are present in equivalent concentrations. This is the case in an ordinary titration, where the quantity of weak (indicator) acid is much smaller than that of the strong acid being titrated, and hence there is practically no indicator neutralized until substantially all of the strong acid is combined with base.

Let us define an indicator provisionally as follows: *An indicator acts like a weak acid which changes its color upon neutralization.* This definition is all that is needed to understand the behavior of an acid-alkali indicator so far as analytical chemistry is concerned. An indicator acts like a weak acid which changes its color when neutralized; with the reverse change of color when it is freed from its salt by a strong acid, of course. However, in view of known relations between the color of organic compounds and their structure, it is necessary that some change in the structure of the complex organic radical take place at the same time as neutralization, such as a rearrangement of its atoms or a change in their linkages. Isomers such as are here concerned are called tautomeric compounds, since they change from one form to another. It is necessary that this change take place immediately upon neutralization of the indicator acid, however, and substances which change color slowly are quite unsuitable for use as indicators. In a very full and detailed discussion of indicators, Noyes[1] considers an indicator as a mixture of two tautomeric acids, HIn′ and HIn″, of which the former is a much weaker acid than the latter. Of course, both of the indicator acids are very weak compared to any acid which is being titrated. The weaker acid HIn′ exists in much larger proportion in acid solutions, and its color determines the "acid color" of the indi-

[1] *J. Am. Chem. Soc.*, **32,** 815 (1910); see also Salm, *Z. physik. Chem.*, **57,** 471 (1906); Rosenstein, *J. Am. Chem. Soc.*, **34,** 1117 (1912); **35,** 1883 (1913).

cator; but upon neutralization, the salt of the stronger acid HIn″ is formed in predominating quantity, and its color determines the "alkaline color" of the indicator. This explains the organic structural side of indicators, since the two groups In′ and In″ have different structures. It seems to be an established fact that the color change of an indicator is the result of some structural rearrangement of its molecule,[1] and that it is not due to association of it into larger molecules, or to any colloidal effect.

The color of a solution of these two tautomeric substances is determined by the relative quantities of them present. As one form predominates in acid solution and the other when the indicator acid has been neutralized, the color is determined by the *fraction* of the indicator which has been changed into its salt. The fraction of an indicator which shows the alkaline color is approximately the fraction of it which exists in the ionized form, since at the small indicator concentrations ordinarily used the indicator salt is practically completely ionized. In the presence of its salt, or in the presence of free strong acid (one or the other is always present), the indicator acid is not appreciably ionized.

In titrations the indicator-acid concentration is very small compared to that of the acid being titrated, and no correction need be applied for the quantity of base acting upon the indicator. As stated above, the end point of a titration as shown by color changes depends upon the relative quantities of indicator acid and indicator salt present in solution. The reaction

$$HIn + KOH = H_2O + KIn$$

takes place to a certain extent, HIn here including both forms of the indicator acid so far as structure is concerned. Let x be the fraction of indicator converted to its alkaline color, *i.e.*, the fraction of it neutralized, and let K_i be the ionization constant of the indicator acid. Then

$$\frac{(H^+)(In^-)}{(HIn)} = K_i,$$

but the concentration of indicator ion (In^-) is x times the total concentration of indicator added, and the remaining indicator

[1] Lifschitz and Beck, *Kolloide-Z.*, **26**, 58 (1920); Birge and Acree, *J. Am. Chem. Soc.*, **41**, 1031 (1919); Sorensen, *Biochem. Z.*, **21**, 131 (1909).

acid is $(1 - x)$ times the indicator concentration. This indicator concentration is commonly not measured, and need not be known, since the ratio $(In^-)/(HIn) = x/(1 - x)$. Substituting this ratio in the ionization equation above, we have

$$(H^+) \frac{x}{(1 - x)} = K_i; \text{ or } (H^+) = K_i \frac{(1 - x)}{x}. \qquad (11)$$

It has been determined, by adding base to solutions containing known quantities of indicator and no other acid, that some indicators change color when only a small fraction has been neutralized, others not until nearly the whole indicator acid has been changed to its salt. Thus phenolphthalein changes its color when x is about one-tenth; methyl orange when nine-tenths of it is neutralized; rosolic acid changes when about one-tenth is neutralized. Since the indicator constants K_i are known for these indicators,[1] the hydrogen ion concentration at the end point may be calculated for each one. For example, K_i is 10^{-10} for phenolphthalein, the color changes when x, the fraction neutralized, is about 0.1, and upon substituting in equation (11)

$$(H^+) = 10^{-10} \frac{0.9}{0.1} = 10^{-9}.$$

Similarly, for rosolic acid ($K_i = 4 \times 10^{-8}$),

$$(H^+) = 4 \times 10^{-8} \frac{0.9}{0.1} = 4 \times 10^{-7}$$

and for methyl orange ($K_i = 5 \times 10^{-4}$),

$$(H^+) = 5 \times 10^{-4} \frac{0.1}{0.9} = 5 \times 10^{-5}.$$

The custom of writing $(H^+) = 10^{-9}$ as pH = 9 or $p_H = 9$ seems to have come into common use, following its introduction among biological chemists by Sorensen. Thus an indicator might be described as having a pH range of 8.3 to 10.0. This means that when the hydrogen ion concentration is $10^{-8.3}$ the indicator shows its acid color, when the hydrogen ion con-

[1] Data for other indicators may be obtained from SALM, *Biochem. Z.*, **21,** 131 (1909); RUPP and LOOSE, *Ber.*, **41,** 3905 (1908); JONES, *J. Am. Chem. Soc.*, **37,** 776, 1694 (1915); TIZARD, *Brit. Assoc. Advancement Sci. Rept.*, **1911,** 268; PRIDEAUX, "Theory of Indicators," p. 137; and from the catalogs of firms dealing in indicators.

centration is 10^{-10} it shows its alkaline color, and in the range between these figures it is undergoing transition. We shall usually follow the custom in use by chemists and state this fact by writing that the hydrogen ion concentration range is 5×10^{-9} to 10^{-10}. Since only one significant figure is known for the indicator constant, results of calculation should be rounded off in the way just illustrated. Thus, to write $(H^+) = 3.6 \times 10^{-7}$ for rosolic acid is not proper, for this indicates that the actual hydrogen ion concentration is known to be between 3.5 and 3.7 $\times 10^{-7}$, and such a statement is not justified by experiment.

The above indicators have long been known and they are the ones most commonly used in analytical chemistry. Modern work has shown that they are less reliable as indicators than a group of sulphonephthaleins which exhibit the behavior of true monobasic acid indicators. Phenolphthalein[1] has long been known to exhibit some of the characteristics of a dibasic acid. The following list, selected by Clark and Lubs,[2] has been recommended for work in biology. One other indicator, brom cresol green,[3] has been included in this list as a substitute for methyl red, which is sometimes reduced irreversibly to a colorless compound.

Indicator	pH range	Color change
Thymol blue	1.2–2.8	Red-yellow
Brom phenol blue	3.0–4.6	Yellow-blue
Methyl red	4.2–6.3	Red-yellow
Brom cresol green	4.0–6.0	Yellow-green
Brom cresol purple	5.2–6.8	Yellow-purple
Brom thymol blue	6.0–7.6	Yellow-blue
Phenol red	6.8–8.4	Yellow-red
Cresol red	7.2–8.8	Yellow-red
Thymol blue	8.0–9.6	Yellow-blue
Ortho cresol phthalein	8.2–9.8	Colorless red

The hydrogen ion concentration in a solution as it approaches the end point in a titration changes much more rapidly when both base and acid are strong than when a weak acid is being

[1] Rosenstein, *J. Am. Chem. Soc.*, **34**, 1117 (1912).

[2] *J. Bact.*, **2**, 1 (1917).

[3] Cohen, Barnett, *Proc. Soc. Exptl. Biol. Med.*, **20**, 124 (1922).

titrated. Table 90 shows the change of hydrogen ion concentration at various stages of titrating 100 c.c. of a strong acid, of acetic acid, and of boric acid.

TABLE 90.—CHANGE OF HYDROGEN ION CONCENTRATION IN TITRATION

Volume of base added (cubic centimeters)	Hydrogen ion concentration		
	Strong acid	Acetic acid $K = 1.8 \times 10^{-5}$	Boric acid $K = 6.6 \times 10^{-10}$
95	6.0×10^{-3}	9.0×10^{-7}	3.0×10^{-11}
98	2.5×10^{-3}	3.6×10^{-7}	1.6×10^{-11}
99	1.2×10^{-3}	1.8×10^{-7}	1.0×10^{-11}
99.5	6.0×10^{-4}	9.0×10^{-8}	8.0×10^{-12}
99.9	1.2×10^{-4}	1.8×10^{-8}	6.0×10^{-12}
100	1.0×10^{-7}	8.0×10^{-10}	5.0×10^{-12}
100.1	8.0×10^{-12}	8.0×10^{-12}	4.0×10^{-12}
100.5	16.0×10^{-13}	16.0×10^{-13}	8.0×10^{-13}
101	8.0×10^{-13}	8.0×10^{-13}	4.0×10^{-13}

It will be seen in this table that when the quantity of 0.5 normal base added to 100 c.c. of 0.5 normal strong acid is 99.9, the hydrogen ion concentration is 1.2×10^{-4}; when 100.1 c.c. of base have been added it is 8×10^{-12}; and that the corresponding figures for boric acid are 6×10^{-12} and 4×10^{-12}. Thus a correct titration of boric acid would involve the use of an indicator changing color in a range of hydrogen ion concentration which is impractically small. Almost any indicator would give a satisfactory end point for the strong acid.

Phenol red and rosolic acid change color at the same hydrogen ion concentration as that which exists in pure water; they show the point at which a solution is really neutral. It does not follow, however, that either indicator is, on that account, suited to a given titration. In analytical chemistry, calculations are based upon the assumption that the acid in a solution is equivalent to the standard base added to it; and this will not be the case in a truly neutral solution if the salt formed is hydrolyzed. In titrating acetic acid, a proper end point is that at which the acid in solution is exactly equivalent to the base added; that is, the end point should come at the hydrogen ion concentration which exists

in potassium acetate solution. From equation (6*a*), page 265,

$$\frac{h^2C}{(1-h)} = \frac{K_w}{K_a} = \frac{10^{-14}}{18 \times 10^{-6}},$$

whence, if the salt at the end point is 0.1 normal, h is 7×10^{-5}, and the concentration of free hydroxide is hC, or 7×10^{-6}. The hydrogen ion concentration may be calculated by dividing this hydroxide ion concentration into 10^{-14}, the ion product for water, and is 1.4×10^{-9}. Thus, the solution is alkaline at the true end point, which should be taken when acid and base are present in equivalent quantity; and phenolphthalein, which changes color at a hydrogen ion concentration of about 10^{-9}, is much better for this titration than an indicator which shows true neutrality.

Suppose it is desired to titrate ammonia, a base whose ionization constant is 18×10^{-6}. Application of equation (7) for the hydrolysis of its salt leads to $h = 7 \times 10^{-5}$, or a concentration of free acid (hydrochloric acid if ammonium chloride is considered) of 7×10^{-6} for 0.1 normal salt solution. There will be this same concentration of free base as well, but in the presence of a large quantity of ammonium salt it does not ionize appreciably. The strong acid may be assumed completely ionized. Thus an indicator which changes color when the hydrogen ion concentration is 7×10^{-6} shows the true end point; methyl orange is suitable.

Rosolic acid, which indicates true neutrality in a solution, is less suited to either of these titrations. When it changes color, the hydrogen ion concentration (and the hydroxide ion concentration as well) is 10^{-7}. Thus in the case of ammonia, since

$$\frac{(NH_4^+)(OH^-)}{(NH_4OH)} = 18 \times 10^{-6}$$

in any solution containing these ions, by inserting 10^{-7} for the hydroxide ion concentration, it follows that the ratio $(NH_4^+)/(NH_4OH)$ is 180, and therefore there remains 1/181 of ammonium hydroxide still to be titrated when this indicator shows an end of the titration, leading to an error of about 0.5 per cent.

If phenolphthalein is used in titrating ammonia with hydrochloric acid, a very serious error results, for when this indicator changes color, the hydrogen ion concentration is about 10^{-9}; hence the hydroxide ion concentration is 10^{-5}, and

$$\frac{(NH_4^+) \times 10^{-5}}{(NH_4OH)} = 18 \times 10^{-6}, \text{ or } \frac{(NH_4^+)}{(NH_4OH)} = 1.8,$$

which shows that only about two-thirds of the base has been titrated. A similar error would result in titrating acetic acid with methyl orange. Thus, we see that it is necessary to select a proper indicator when weak acids or weak bases are involved. For such a titration as nitric or sulfuric acid with sodium hydroxide, where there is no appreciable hydrolysis of the salt formed, any indicator will give reliable results.

Titration of Dibasic Acids and Their Salts.[1]—Let us consider as an example the titration of a mixture of sodium carbonate and sodium bicarbonate. Phenolphthalein is commonly considered to show the point at which all normal carbonate has been converted to bicarbonate, while the bicarbonate originally present in solution is unchanged.

In the titration of soda ash, the end point is commonly taken as the point where the pink color disappears completely. Under laboratory conditions the color of phenolphthalein becomes invisible when about 3 per cent of it remains in the colored (salt) form; and since K_i is 10^{-10} and x is 0.03, $(H^+) = K_i(1 - x)/x = 3 \times 10^{-9}$. Upon substituting this hydrogen ion concentration into the ionization expressions for carbonic acid it is found that

$$\frac{(HCO_3^-)}{(H_2CO_3)} = \frac{100}{0.8} \text{ and } \frac{(CO_3^{--})}{(HCO_3^-)} = \frac{1.6}{100}.$$

If no bicarbonate had been changed to carbonic acid, the ratio $(HCO_3^-)/(H_2CO_3)$ should be infinite, and in the above calculation it is 100 to 0.8, which means that 0.8 per cent of the bicarbonate has been transformed to free carbonic acid, at the expense of an equivalent amount of standard acid. On the other hand, if the titration of carbonate to bicarbonate were complete, the ratio $(CO_3^=)/(HCO_3^-)$ should be zero, since no carbonate should remain unchanged. The fact that at the end point this ratio is 0.016 shows that 1.6 per cent of the carbonate is still untransformed. Since the second of these errors corresponds to stopping short of the end point by 1.6 per cent and the first corresponds to overrunning the end point by 0.8 per cent, the net error of the process is 0.8 per cent. This calculation is based upon the assumption that the solutions remain cold. If the titration is carried out

[1] In this connection, read again the paragraph on ionization of dibasic acids, page 260.

near the boiling temperature, the bicarbonate decomposes almost as fast as formed and a permanent discharge of the pink color corresponds to conversion of sodium carbonate into sodium chloride.

Change of Chemical Equilibrium with Temperature.—When any chemical system at equilibrium is heated, the chemical reaction proceeds in the direction which absorbs heat. For example, neutralization of an acid by a base evolves heat, hydrolysis (the reverse process) absorbs heat; hence when a salt solution is heated, the fraction hydrolyzed increases. Similarly, the union of hydrogen and oxygen to form water vapor, the union of carbon monoxide and oxygen to form carbon dioxide, and the union of hydrogen atoms into molecules all evolve large quantities of heat. Heat would, therefore, be required to tear these molecules apart, and an increase of temperature (*i.e.*, absorption of heat by the system at equilibrium) is attended by an increase in the fraction dissociated. Table 91 shows this effect at 1-atmosphere pressure.

TABLE 91.—PERCENTAGE DISSOCIATION OF GASES[1]

T_{abs}	H_2O	CO_2	H_2
1,000	0.000028	0.0002	
1,200	0.000745	0.0093	
1,400	0.00787	0.146	
1,600	0.0446	0.110	
1,800	0.1700	0.546	
1,900	0.302	1.04	
2,000	0.504	1.84	0.33
2,200	1.21	5.0	0.92
2,500	3.38	15.6	3.15
3,000	11.1	48.5	13
3,500	.....	.....	34
4,000	.....	.....	61

There is a quantitative relation between the heat of a reaction and the change of its equilibrium constant with temperature. Before giving this equation, it is necessary to mention again the convention followed in writing expressions for chemical equilibrium. First the chemical reaction should be written down,

[1] LANGMUIR, *J. Am. Chem. Soc.*, **28**, 1357 (1906); **37**, 417 (1915).

the appropriate change in heat content, ΔH, corresponding to it should be computed, then the equilibrium expression should be written with the products of the reaction in the numerator. It is, of course, permissible to write the chemical reaction in either way; thus

$$2H_1 = H_2; \Delta H = -90{,}000 \text{ cal.},$$

or

$$H_2 = 2H_1; \Delta H = 90{,}000 \text{ cal.},$$

provided the equilibrium expression is written $p_{H_2}/p^2_{H_1} = K$ to correspond to the first way of writing the chemical reaction and $p^2_{H_1}/p_{H_2} = K$ if the reaction is written in the second way. Corresponding to the second way, ΔH is $+90{,}000$ cal., and the change of equilibrium constant with temperature is shown by the differential equation[1]

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2}, \tag{12}$$

which is called the van't Hoff equation.[2] By means of this equation the equilibrium constant at any temperature can be calculated from that at another temperature if the heat absorbed by the chemical reaction is known, or the heat absorption may be calculated from equilibrium constants at two different temperatures. If the heat effect does not change appreciably over the temperature interval involved, this equation may be integrated between limits, and becomes

$$2.303 \log \frac{K_2}{K_1} = \frac{\Delta H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right], \tag{13}$$

where 2.303 is the conversion factor from natural to ordinary logarithms. In using this equation, R is expressed in calories

[1] As in other cases, *ln* is here used to indicate natural logarithms; those to the base 10 are indicated by the abbreviation *log*.

[2] This equation may be derived from the laws of thermodynamics for a system of ideal gases or ideal solutes by a process similar to that which gave the Clausius-Clapeyron equation, derived on page 78. It can be seen that the Clausius-Clapeyron equation is a special case of the van't Hoff equation for the equilibrium constant of the physical reaction

$$H_2O \text{ (liq.)} = H_2O \text{ (vapor)}.$$

The quantity ΔH for this reaction is the latent heat of evaporation, and the equilibrium constant would be written $p = K$. The van't Hoff equation differs from the Clapeyron equation in having the equilibrium constant for a chemical process in place of that for a change in state of aggregation.

if the heat of reaction is so expressed. Since the equilibrium constants appear in this equation as a ratio, any units may be used in formulating them, provided the same units are employed at both temperatures. Thus if the partial pressures are in millimeters of mercury in one case, they must be in the other also.

Let x be the fractional dissociation of hydrogen into atoms; for each mol of hydrogen composing the equilibrium mixture at a low temperature, x mols dissociate at 3000°, forming $2x$ mols of H_1, and there remain $(1 - x)$ mols of H_2. Then the mol fraction of H_1 is $2x/(1 + x)$, and the mol fraction of H_2 is $(1 - x)/(1 + x)$. When the total pressure is 1 atmosphere, the partial pressures in atmospheres are equal to the mol fractions, and the dissociation constant is

$$\frac{(2x)^2/(1 + x)^2}{(1 - x)/(1 + x)} = K = \frac{4x^2}{1 - x^2}.$$

At 3000° absolute and 1 atmosphere, $x = 0.13$ and $K = 0.0686$ as calculated on page 248. It is desired to calculate the dissociation constant and the fractional dissociation at 3500° absolute. Upon substituting 0.0686 for K_1, 3000 for T_1, 3500 for T_2 and 90,000 cal. for ΔH, into equation (13), K_2 is found to be 0.59; and since this is equal to $4x^2/(1 - x^2)$, x is 0.36. The result of experiment is 34 per cent dissociation at 3500° abolute, and 1-atmosphere pressure. This deviation is due in part to our assumption that ΔH remains constant over the temperature range 3000 to 3500°, which is not quite the case. It would be better to express ΔH as a function of the temperature, as was explained on page 239, and substitute this expression into equation (12) before integrating it between temperature limits.

Let us consider an equilibrium in which the heat of reaction changes considerably with the temperature, namely, $2CO_2 = 2CO + O_2$ for which ΔH is 136,000 cal. at 20°. From equation (7) (page 239) $d(\Delta H) = \Delta C_p dT$. The heat capacity of carbon dioxide may be taken as $7.0 + 0.0028T$ cal. per mol per degree, that for carbon monoxide and oxygen $6.5 + 0.001T$ cal. per mol per degree. Then the increase in heat capacity, ΔC_p, is $3(6.5 + 0.001T) - 2(7.0 + 0.0028T)$, or $\Delta C_p = 5.5 - 0.0026T$. Substituting in the equation above, and integrating,

$$\Delta H = 5.5T - 0.0013T^2 + I,$$

where I is an integration constant. When T is 293 (*i.e.*, at 20°C.), ΔH is 136,000, whence the integration constant is 134,500, and the value of ΔH to be inserted in van't Hoff's equation is $134{,}500 + 5.5T - 0.0013T^2$. Then

$$d \ln K = \left(\frac{134{,}500 + 5.5T - 0.0013T^2}{RT^2}\right) dT$$

and, upon integration, since R is 1.99 cal.,

$$\ln \frac{K_2}{K_1} = 67{,}600 \left(\frac{1}{T_1} - \frac{1}{T_2}\right) + 2.8 \ln \frac{T_2}{T_1} - 0.0007(T_2 - T_1).$$

Suppose it is desired to calculate the equilibrium constant at 2500° absolute from that at 2200° absolute; by inserting these temperatures in the above equation, converting to ordinary logarithms and solving, we find that K_{2500}/K_{2200} is 46.

Let x be the fractional dissociation. Then for 2 mols of CO_2 in the system at room temperature, there will be $2x$ mols dissociated at the temperature T, hence $2x$ mols of carbon monoxide formed, x mols of oxygen, and $2 - 2x$ mols of carbon dioxide remaining. The total number of mols is $2x + x + (2 - 2x)$ or $2 + x$, and the partial pressures when the total pressure is 1 atmosphere are, therefore, $2x/(2 + x)$ for carbon monoxide, $x/(2 + x)$ for oxygen, and $(2 - x)/(2 + x)$ for carbon dioxide. The equilibrium expression corresponding to $2CO_2 = 2CO + O_2$ is

$$K = \frac{p^2_{CO} \cdot p_{O_2}}{p^2_{CO_2}} = \frac{\left(\frac{2x}{2 + x}\right)^2 \frac{x}{(2 + x)}}{\left(\frac{2 - 2x}{2 + x}\right)^2} = \frac{4x^3}{(2 - 2x)^2(2 + x)}.$$

At 2200°, x is 0.05, whence K_{2200} is 67×10^{-6}; by the calculation above, K_{2500} is 46 times this, or 3150×10^{-6}. Then upon solving the equation

$$K_{2500} = \frac{4x^3}{(2 - 2x)^2(2 + x)} = 3150 \times 10^{-6},$$

the fractional dissociation of carbon dioxide at 2500° absolute is obtained. It is not necessary to apply a general solution for cubics to this problem, however. By estimating values of x and substituting them into the equation it is found that $x = 0.16$ gives a smaller value to the left-hand side than 3150×10^{-6},

while $x = 0.17$ gives a larger value. The dissociation is therefore about 16 per cent; direct experiment gives 15.6 per cent.

When the temperature range over which a calculation is to be made is small, the heat of reaction may be assumed constant, thus avoiding the extra calculation involved in the case just explained. It should be remembered, however, that in many cases the heat of a reaction at two different temperatures is quite different, and that calculations assuming it constant are liable to be in error.

For approximate calculations it is sometimes sufficient to calculate the heat of a reaction at each of the two temperatures involved in a calculation, assume that the average of these two values is a sufficient representation of ΔH over the whole range, and employ the simple integrated van't Hoff equation (11). But the van't Hoff equation should not be applied over a range of temperature such that some of the substances involved are vapors at the higher temperature and liquids or solids at the lower temperature. Under these conditions the heat of reaction undergoes a sudden change with temperature which cannot be represented by a simple equation.

Questions

Numerical data should be sought in the tables in the text

1. When a mixture of 1 mol of HCl and 0.48 mol of oxygen is brought to equilibrium according to the Deacon process reaction $4HCl + O_2 = 2H_2O + 2Cl_2$ at 386°, it is found that 0.402 mol of chlorine has been formed. Calculate the partial pressure of each gas in the equilibrium mixture when the total pressure is 1 atmosphere, and calculate the equilibrium constant.

Ans. $K = 80$.

2. From the data of the previous problem, calculate the yield of chlorine when a mol of HCl and a mol of oxygen are heated to equilibrium at 386° and 1 atmosphere. (Formulate the partial pressures in terms of x, the fraction of HCl oxidized to chlorine, and solve the resulting equation by trial.)

3. The equilibrium constant of the Deacon process reaction is 80 at 386° and 296 at 352°. Calculate how much heat is absorbed by the reaction per mol of chlorine produced. Calculate the equilibrium constant at 419°.

Ans. $K = 25$.

4. Potassium cyanide is 3.6 per cent hydrolyzed in 0.1 formal solution at 50°. Calculate the ionization constant of water at this temperature. The ionization constant of hydrocyanic acid is 7×10^{-10}.

5. Phosgene is 80 per cent dissociated into carbon monoxide and chlorine at 550° and 91 per cent dissociated at 600°. Calculate the heat of dissocia-

tion, and make clear whether heat is evolved or absorbed upon dissociation.

6. When a mol of hydrogen dissociates at 3000° absolute, 90,000 cal. of heat are absorbed. Calculate the fractional dissociation at 2200° from the fact that at 3000° hydrogen is 13 per cent dissociated into atoms. Assume a constant heat of reaction.

7. The equilibrium constant of the reaction $CO_2 + H_2 = CO + H_2O$ is 1.2 at 886°C. and 1.59 at 986°. Calculate the heat absorbed by this reaction, assuming it to be constant over the whole temperature range. From this heat absorption, calculate the equilibrium constant at 786° or at 1086°. The measured constant at 1086 is 1.96, and at 786 it is 0.84.

8. A small amount of phenolphthalein is added to a solution prepared by mixing 20 c.c. of 0.1 normal NH_4Cl with 3 c.c. of 0.1 normal NH_4OH. Calculate the hydrogen ion concentration in solution, and the fraction of the indicator transformed to the pink form. $K_i = 10^{-10}$.

9. A solution 0.1 formal in phosphoric acid is titrated with NaOH, using methyl orange as indicator, and the end point is taken when 91 per cent of the indicator shows the alkaline color. The ionization constants of H_3PO_4 are $K_1 = 10^{-2}$, $K_2 = 2 \times 10^{-7}$, $K_3 = 3.6 \times 10^{-13}$. (*a*) Calculate the hydrogen ion concentration at the end point. (*b*) Calculate what fraction of the acid has been converted into NaH_2PO_4. (*c*) What fraction has been converted into Na_2HPO_4?

10. The 0.1 formal H_3PO_4 is titrated with NaOH, using phenolphthal
as indicator, and the end point is taken when 5 per cent of the indica
changed to pink. (*a*) Calculate (H^+), the ratio $(H_2PO_4^-)/(HPO_
ratio $(HPO_4^{--})/(PO_4^{---})$ corresponding to this end p
NaOH (0.10 normal) would be required for the titratio

11. To 100 c.c. of 0.1 normal sodium acetate at 25°
of benzoic acid ($C_6H_5CO_2H$). The ionization cons
18×10^{-6}, that for benzoic acid is 60×10^{-6}. C
base combined with each acid at equilibrium.

12. The equilibrium constant of the reactio
527° is 15.5×10^{-6} and at 627° it is $3.16 \times$
absorbed in the reaction. Calculate the equilib

13. To a solution 0.1 formal in KNO_2 and 0.
equal volume of 0.1 formal HCl. Calculate th
acid.

14. Calculate the hydrolysis of 0.1 formal

15. If a liter of 0.1 formal ammonium for
formal acetic acid, what fraction of the salt
What will be the fraction converted to aceta
solutions is added to three liters of water?

16. How much sodium acetate must b
acetic acid to reduce hydrogen ion concen
value?

17. When 1 gram of water is placed in
with liquid sulfur, the reaction $2H_2O$
From the value of the equilibrium constar

calculate the partial pressures of each substance at equilibrium. Calculate what fraction of the water is converted into hydrogen sulfide.

18. A mixture of 1 mol of carbon dioxide and 3 mols of hydrogen is heated at 986° until equilibrium is established. Calculate the partial pressure of each gas in the equilibrium mixture. The equilibrium constant is 1.59 for the reaction $CO_2 + H_2 = H_2O + CO$.

19. Sodium phenolate is 5.6 per cent hydrolyzed at 25° in 0.03 formal solution. Calculate the hydrolysis constant and the ionization constant of phenol as an acid.

20. The sodium salt of mesitol is 13.8 per cent hydrolyzed in 0.03 formal solution. Calculate its ionization constant as an acid. If 0.01 formula weight of sodium hydroxide is added to a solution 0.01 formal in phenol and 0.01 formal in mesitol, what fraction of each acid will be neutralized?

21. (*a*) Calculate the hydrogen ion concentration at the correct end point for 0.2 normal NH_4OH titrated with 0.2 normal HCl. (*b*) Calculate also the hydrogen ion concentration when the end point is 0.1 per cent short of the true one and when it is 0.1 per cent overstepped. (*c*) Calculate the upper and lower limits for the indicator constant if it is assumed 9 per cent in its alkaline form at the end point.

22. The heat of neutralization of ammonia by acetic acid is $\Delta H = -25{,}000 + 48T$. (*a*) Calculate the hydrolysis of 0.1 formal ammonium tate at 75° from the fact that it is 0.5 per cent hydrolyzed at 25°. (*b*) The ation constant for NH_4OH at 75° is 15×10^{-6} and that for acetic acid $^{-6}$. Calculate the ionization constant of water at 75°.

e the hydrogen ion concentration in solutions formed normal acetic acid is titrated with 99, 99.8, 100, and sodium hydroxide. (*b*) What percentage error results ranitrophenol ($K_i = 10^{-7}$) is the indicator and 20 kaline form at the end point? (*c*) What percentage he use of thymol blue (K_i is about 10^{-9}) when 9 per n?

acid ($K = 1.8 \times 10^{-5}$) and HCl is titrated with ethyl orange ($K_i = 5 \times 10^{-4}$; $x = 0.80$); and n. The first titration requires 39 c.c. of 0.10 mixture and the second requires 75 c.c. Calcu- rated in the methyl orange titration and the the original mixture, assuming both acids are nd titration.

constant of the reaction $H_2 + C_2H_2 = C_2H_4$ atmospheres. Calculate the total pressure t dissociated at 750°.

ing PCl_5 to 200° weighs 3.6 grams per liter sphere. Calculate the partial pressure of l the fractional dissociation of PCl_5.

and 1 gram of hydrogen are heated to mixture matches in color a similar vessel ic. Calculate the fraction of the hydrogen

onverted to HI and the equilibrium constant of the reaction $H_2 + I_2 =$ HI.

28. Sodium carbonate is titrated with HCl, and phenolphthalein ($K_i =$ 0^{-10}) as indicator. The ionization constants for H_2CO_3 are $K_1 = 3.5 \times 10^{-7}$ nd $K_2 = 5.4 \times 10^{-11}$. Calculate the hydrogen ion concentration when per cent (pink), 5 per cent (faint pink), and 2 per cent (colorless) f the indicator remain in the alkaline form. Calculate the ratios $CO_3^{--})/(HCO_3^-)$ and $(H_2CO_3)/(H_2CO_3^-)$ at each end point, and from them he net error in taking each color as the end of the titration.

CHAPTER IX

HETEROGENEOUS EQUILIBRIUM

We have so far considered equilibrium in a single phase, either gas or solution. In many cases, the equilibrium conditions in a given phase are closely related to those in another phase; often they are fixed completely by the presence of a solid in excess. Thus the concentration of a solution which at any given temperature is in equilibrium with the solid solute is determined by the solubility of that solute.

Some examples of two-phase equilibrium have been studied in earlier chapters, where a solid present in excess fixed the concentration or pressure in a gaseous phase or in a solution. The partial pressure of a solute above a solution is fixed by its concentration in the solution (Henry's law), the vapor pressure of a solution at a fixed temperature is proportional to the mol fraction of solvent (Raoult's law), the concentration of solute in one liquid phase fixes that in another liquid in equilibrium with it (distribution law), and the equilibrium between a solution and solid solvent is established according to the freezing-point laws. This chapter is mainly concerned with similar aspects of equilibrium when more than one phase is present.

Solids and Gases.—When gases react with solids to produce other solids and gases, the equilibrium is formulated (after writing the chemical reaction) in the same way as for other equilibria, except that the partial pressures or concentrations of solid substances are left out entirely. This is equivalent to including all of these partial pressures in the numerical value of the equilibrium constant, and allows the formulation of equilibria when these partial pressures (sublimation pressures) are not capable of determination. Thus in the reaction

$$Ag_2S\ (\text{solid}) + H_2 = 2Ag(\text{solid}) + H_2S,$$

it is not necessary to write

$$\frac{p^2_{Ag}p_{H_2S}}{p_{Ag_2S}p_{H_2}} = K',$$

for the sublimation pressures of these solids are too small for experimental determination. In the presence of each solid, the partial pressure of it above the solid is constant so long as the temperature remains constant, and we may, therefore, write

$$p_{H_2S}/p_{H_2} = K$$

to represent this equilibrium, where K is the product of K' and the ratio of two constant sublimation pressures for silver and silver sulfide, *i.e.*, $K = K'p_{Ag_2S}/p^2_{Ag}$. Indeed, it has not been established that there is any silver or silver sulfide present in the gaseous phase at all, but experiment shows that when silver sulfide and hydrogen are brought together at any temperature, the ratio of the partial pressure of hydrogen sulfide to hydrogen is constant at equilibrium in the presence of both solids, regardless of the quantities of each employed; and that this same ratio is established when silver and hydrogen sulfide are brought together in any quantity, though the quantities of the two solids remaining at equilibrium may be in any ratio whatever.

Thus at 476° the ratio of the partial pressure of hydrogen sulfide to hydrogen[1] is 0.359 at equilibrium, *provided both solid substances are present.* It is important to remember that the equilibrium ratio $p_{H_2S}/p_{H_2} = K$, while it does not contain any written reference to silver or silver sulfide, refers only to the equilibrium between *these two solids* and the two gases. If a mol of silver sulfide were put into contact with 10 mols of hydrogen, there would be formed 1 mol of hydrogen sulfide and 9 of hydrogen would remain, but no silver sulfide would be present. This condition is one of true chemical equilibrium, but it is not the equilibrium to which the constant ratio of hydrogen sulfide to hydrogen applies. The limiting ratio of the two substances in order to establish this equilibrium is 1 mol of hydrogen to 0.264 mol of silver sulfide, for by reaction this would produce 0.264 mol of hydrogen sulfide and $1 - 0.264$, or 0.736, mol of hydrogen would remain. These mol fractions in the gas mixture are in the ratio 0.359, and any quantity of silver sulfide greater than 0.264 formula weights per mol of hydrogen would, therefore, suffice to establish equilibrium with all four substances present. Any smaller quantity of silver sulfide per mol of hydrogen would be

[1] F. G. Keyes and Felsing, *J. Am. Chem. Soc.*, **42,** 246 (1920).

completely reduced without raising the ratio p_{H_2S}/p_{H_2} to the equilibrium value of this temperature. Similarly, the least quantity of hydrogen which would suffice to reduce completely one formula weight of silver sulfide at 476° is 1 mol for the actual chemical process plus (1/0.359 = 2.79) mols to maintain the equilibrium ratio, or a total of 3.79 mols. If a smaller quantity of hydrogen reacts upon a formula weight of silver sulfide, equilibrium is established in the gaseous phase before all of the sulfide is reduced; if a larger quantity of hydrogen is employed, complete reaction takes place without forming enough hydrogen sulfide to produce the equilibrium ratio of partial pressures.

As with homogeneous equilibrium, that in which several phases are involved changes with the temperature. In the example just considered, the ratio of hydrogen sulfide to hydrogen at equilibrium is as follows:

TABLE 92.—EQUILIBRIUM CONSTANTS AT DIFFERENT TEMPERATURES

Centigrade temperature	Equilibrium constant
476	0.359
518	0.325
617	0.278

The van't Hoff equation may be applied to heterogeneous equilibria in the same way as to reactions taking place in a single phase, to calculate the equilibrium at one temperature from that at another when the heat of reaction is known, or to calculate the heat absorbed from equilibrium constants at two different temperatures. Thus, to calculate the heat absorbed in a reaction,

$$2.303 \log \frac{K_2}{K_1} = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right).$$

And by substituting 0.359 for K_1 and 476 + 273 for T_1, 0.278 for K_2 and 617 + 273 for T_2, we find that $\Delta H = -2410$ cal., or

Ag_2S (solid) + H_2 = 2Ag (solid) + H_2S; $\Delta H = -2410$ cal.

Dissociation Pressures.—When a solid decomposes to form another solid and a gas, the equilibrium constant of the reaction is the pressure of the gas. Thus for the reaction

$$CaCO_3 \text{ (solid)} = CaO \text{ (solid)} + CO_2,$$

the equilibrium expression is $p_{CO_2} = K$.

In many cases a solid upon evaporation forms two or more gases; for example,

$$NH_4Br \text{ (solid)} = NH_3 + HBr + NH_4Br \text{ (vapor)},$$

for which the mass-action expression is $p_{NH_3} \cdot p_{HBr} = K$. As usual, the partial pressure of ammonium bromide is included in the value of K for the temperature in question. In some cases, such as ammonium hydrogen sulfide (NH_4HS), complete dissociation occurs in the vapor phase, in which case each partial pressure is half of the total dissociation pressure. In cases such as that of ammonium bromide, dissociation is incomplete, and the extent of this dissociation must be determined from vapor-density measurements or in some other suitable way. From the change of equilibrium with temperature the heat effect of the reaction can be computed in the same way as for homogeneous equilibrium. The heat effect so computed is the heat of the *complete* reaction NH_4Br (solid) = $NH_3 + HBr$, not the effect which would be observed if a formula weight of solid salt at the temperature in question were allowed to undergo the incomplete reaction corresponding to equilibrium. This same statement, of course, applies to any change of equilibrium with temperature computed from the van't Hoff equation. Table 93 shows some experimental results. It will be noted that the equilibrium constant changes rapidly as the temperature increases.

TABLE 93.—DISSOCIATION PRESSURES OF AMMONIUM BROMIDE[1]

Temperature	Pressure $NH_3 = HBr$, mm.	Pressure NH_4Br mm.	Total pressure mm.	Per cent dissociated	$K = pNH_3 pHBr$
320	28.5	43.6	100.6	39.3	812
330	34.6	65.5	134.7	34.9	1,200
340	42.0	94.8	178.8	30.6	1,765
350	49.4	137.7	236.6	26.3	2,440
360	55.7	199.	310.4	22.0	3,100
370	61.0	282.9	404.8	17.7	3,720
380	62.0	400.5	525.5	13.4	3,840

[1] SMITH and LOMBARD, *J. Am. Chem. Soc.*, **37**, 38 (1915).

Two interesting phenomena are here taking place side by side: an increase in the vapor pressure of solid ammonium bromide, and a tendency toward increased dissociation at higher temperatures. The former of these effects largely increases the total pressure, but an increase of total pressure drives back the dissociation to such an extent that there is a decrease in fractional dissociation of *saturated* ammonium bromide vapor with increasing temperatures. For a constant total pressure there would be an increased dissociation at higher temperatures, as in the case of other dissociation reactions.

Distribution between Two Liquids.—The case in which a solute has the same molecular weight in both solvents has been described on page 136, where it was seen that the ratio of the concentration in one liquid to that in the other was constant. In many cases there is a dissociation into simpler molecules upon passage from one solvent to another, and the simple distribution ratio does not apply. For example, benzoic acid exists in water as single molecules which are not ionized to any great extent, and in benzene it is almost entirely associated into double molecules $(C_6H_5COOH)_2$. Passage from one phase to the other is attended by a chemical reaction, the equation for which is

$$2C_6H_5COOH = (C_6H_5COOH)_2;$$

accordingly, the equilibrium is shown by the relation

$$\frac{C_{\text{benzol}}}{C^2_{\text{water}}} = K.$$

The following table shows that this method of formulation represents the facts as determined by experiment, while the simple distribution law does not hold even approximately.

A similar behavior is shown by most organic acids when distributed between water and hydrocarbons. For example, when picric acid is distributed between water and toluene,[1] the ratio of concentrations changes from 6.6 to 14.9; but the equilibrium ratio as formulated between the concentration in toluene and the square of the concentration in water leads to a more satisfactory constant.

[1] *Ber.*, **37,** 4746 (1904); Rothmund and Drucker, *Z. physik. Chem.*, **46,** 827 (1903).

TABLE 94.—DISTRIBUTION OF BENZOIC ACID BETWEEN WATER AND BENZENE AT 20°

Molal concentration		C_b/C_w	C_b/C_w^2
in water	in benzene		
0.0075	0.0084	1.12	150
0.0093	0.0131	1.41	152
0.0125	0.0239	1.92	154
0.0167	0.0437	2.62	153
0.0210	0.0651	3.10	148
0.0327	0.165	5.05	154
0.0429	0.295	6.90	160

There are other cases in which the distribution ratio changes with the concentration of distributed solute which cannot be explained by simple association in one phase or the other; they must be added to the long list of unexplained phenomena in connection with solutions which are set down as "deviations from the laws of ideal solutes," and which should be called *failure of* the laws of ideal solutions. In such cases, the concentration in one phase may be plotted against that in the second phase from several points determined by experiment, and this empirical curve may then be used in determining other concentrations in one phase when that in the second phase is known.

Solids and Dissolved Substances.—The simplest case of equilibrium between a solid and a dissolved substance is that of a saturated solution of a substance which does not ionize upon solution, the concentration of which solution depends upon the temperature alone.[1] For a given temperature the equilibrium expression is $C = K$, where C is the concentration of the substance. From the solubility at two temperatures not too far apart the heat of solution *into the saturated solution* may be calculated from the van't Hoff equation. This will not be the heat effect of solution of a mol of the substance in a large quantity of water unless its heat of dilution is very small. The equilib-

[1] Strictly speaking, it depends upon the pressure as well, but the small changes in atmospheric pressure produce only a negligible effect which need not be taken into consideration.

rium recation is the passage of molecules of the solute from the solid state into a saturated solution, and a calculation of the heat of reaction from equilibrium constants can give only the heat effect corresponding to the reaction which actually occurs. The heat effect so obtained, plus the heat effect of adding this saturated solution to a large quantity of water, is equal to the heat effect of adding the same quantity of solid to a large quantity of water in the first place (law of constant heat summation).

When a slightly ionized substance, such as benzoic acid, is in equilibrium with its solid phase, the concentration of non-ionized molecules in the solution is constant. According to the mass-action law, the expression $(H^+)(Bz^-)/(HBz) = K$ is also true for all solutions containing these ions and molecules, where HBz is benzoic acid, and Bz is benzoate ion. Upon clearing this expression of fractions, we have $(H^+)(Bz^-) = K(HBz) =$ const. This is a statement of the law of solubility product, which says that in a saturated solution the product of the ion concentrations is a constant for a simple binary electrolyte, *i.e.*, one which gives one positive ion and one negative ion upon ionization. According to this law, the addition of a little nitric acid or hydrochloric acid to a solution saturated with benzoic acid should decrease the concentration of benzoate ions in solution, by forcing them to combine with hydrogen ions and form non-ionized molecules, and cause precipitation of the benzoic acid formed. But as benzoic acid in its saturated solution (0.026 formal) is only 4 per cent ionized, removal of practically all of its ions would decrease the solubility only 4 per cent. The nitric acid would have no effect on the concentration of non-ionized molecules; hence only a small precipitation results from the addition of a strong acid in moderate amount, though the concentration of benzoate ions may be reduced to a hundredth of its former value. A small quantity of sodium benzoate would also produce this effect; it would greatly decrease the hydrogen ion concentration, but produce only a small effect on the total quantity of benzoic acid in solution.

Solubility Product for Ionized Substances.—Experiment shows that the ion-concentration product or solubility product is nearly constant for many slightly soluble salts in the presence of an added salt with one ion in common. In accordance with the

convention already adopted, the concentrations of non-ionized molecules of largely ionized substances are not included in equilibrium expressions, and the activity of the ions is represented by the salt concentration. When silver acetate is dissolved in water, the reaction is written

$$AgAc\ (solid) = Ag^+ + Ac^-$$

and the equilibrium expression is

$$(Ag^+)(Ac^-) = K.$$

Addition of any ionized acetate to the solution decreases the solubility, since an increase in the acetate ion concentration must be attended by a corresponding decrease in the silver ion concentration. This decrease is brought about through combination of silver ions with acetate ions, followed by precipitation. Table 95[1] shows the effect of sodium acetate upon the solubility of silver acetate. It will be observed that the solubility product is roughly constant. Deviations of the kind shown in the last column are to be expected in applying the law of constant solubility product to concentrations as high as 0.2 normal.

TABLE 95.—SOLUBILITY OF SILVER ACETATE IN SODIUM ACETATE SOLUTIONS

Concentration of sodium acetate	Concentration of silver acetate	Solubility product
0	0.0603	37.0×10^{-4}
0.061	0.0392	39.2
0.119	0.0280	41.0
0.239	0.0208	54.0

The solubility of thallous chloride in the presence of potassium chloride and of thallous nitrate is shown in Table 96.

It will be seen from this table that equivalent solutions of a chloride and a thallous salt produce about the same decrease in solubility. The further fact that one chloride has about the same effect as another chloride at an equivalent concentration is illustrated by the data of Table 96*a*.

[1] STIEGLITZ, *J. Am. Chem. Soc.*, **30**, 946 (1908).

TABLE 96.—SOLUBILITY OF THALLOUS CHLORIDE AT 25° IN THE PRESENCE OF POTASSIUM CHLORIDE OR THALLOUS NITRATE[1]

Concentration of added salt		Solubility of TlCl	$(Tl^+)(Cl^-) = K$
$TlNO_3$	KCl		
0	.....	0.01607	25.8×10^{-5}
0.025	.....	0.00880	29.8
0.050	.....	0.00624	35.0
0.100	.....	0.00422	44.0
.....	0.025	0.00869	29.3
.....	0.050	0.00590	33.0
.....	0.100	0.00396	41.1
.....	0.200	0.00268	54.5

TABLE 96*a*.—SOLUBILITY OF THALLOUS CHLORIDE IN THE PRESENCE OF CHLORIDES
(Equivalents per thousand liters)

Concentration of added salt	Measured solubility in the presence of				
	HCl	KCl	$BaCl_2$	$TlNO_3$	Tl_2SO_4
25	8.66	8.69	8.98	8.80	8.9
50	5.83	5.90	6.18	6.24	6.77
100	3.83	3.96	4.16	4.22	4.68
200	2.53	2.68	2.82		

The variation in ion-concentration product with total salt concentration for both silver acetate and thallous chloride shows quite clearly that the simple expedient of employing salt concentration for ion activity is not correct. Since the activity of non-ionized molecules is kept constant by the presence of solid salt, the *ion-activity product* is constant by definition. In other words, the activities of the ions of thallous chloride are such that their product remains constant. Brönsted and La Mer[2] have used solubility data to calculate activity coefficients, employing the Debye-Hückel theory.

In place of following their procedure, let us assume as a reasonable approximation that in a mixture of thallous chloride and

[1] The data quoted from BRAY, *J. Am. Chem. Soc.*, **33**, 1674 (1911).

[2] *J. Am. Chem. Soc.*, **46**, 555 (1924).

potassium chloride the activity coefficient for each ion is the same as that for chloride ions in a solution of potassium chloride at the same *total* concentration (page 211). The data of Table 96 would then be treated as illustrated in Table 97. From the figures in the last column it is evident that our simple assumption

TABLE 97.—ACTIVITY PRODUCT FOR THALLOUS CHLORIDE

Analysis of solution		Activity coefficient	a_{Tl}	a_{Cl}	Activity product
Total Tl	Total Cl				
0.01607	0.01607	0.88	0.0141	0.0141	2.01×10^{-4}
0.0338	0.00880	0.84	0.0284	0.0074	2.10
0.0562	0.00624	0.81	0.0456	0.0050	2.31
0.1042	0.00422	0.76	0.0792	0.00321	2.54
0.00869	0.0337	0.84	0.0073	0.0283	2.07
0.00590	0.0559	0.81	0.00477	0.0452	2.16
0.00396	0.104	0.76	0.0030	0.0790	2.37
0.00268	0.2027	0.71	0.00190	0.144	2.73

regarding activity coefficients in mixtures leads to no satisfactory improvement over the use of salt molality for ion activity. Until such time as *measured* activity coefficients are available for mixtures, it seems best to use salt molality as a rough approximation for activity in mixtures of salts.

The experimental fact that the solubility of thallous chloride is increased by small additions of potassium nitrate might be taken as evidence that non-ionized molecules of salts form by metathesis, $TlCl + KNO_3 = TlNO_3 + KCl$. But if the conductance ratio is taken as a measure of fractional ionization, and $C\Lambda/\Lambda_0$ as the ion concentration in the mixtures in Table 96, the "ion-concentration product" is still far from constant. It increases from 20.4×10^{-5} in the absence of added salt to 29.0×10^{-5} for 0.2 normal KCl. At least, if ionization is incomplete, the conductance ratio Λ/Λ_0 is not a satisfactory measure of its incompleteness.

Reactions between Solids and Dissolved Substances.—Equilibrium between ferrous carbonate and dissolved carbon dioxide according to the reaction

$$FeCO_3 \text{ (solid)} + H_2CO_3 = Fe(HCO_3)_2$$

has been studied over a wide range of concentration,[1] and the equilibrium expression is

$$\frac{(Fe^{++})(HCO_3^-)^2}{(H_2CO_3)} = K.$$

Let S denote the solubility of ferrous salt in the carbonic acid solutions, *i.e.*, its molal concentration in carbonic acid solution in equilibrium with solid ferrous carbonate, as determined by titration of a portion of the saturated solution. Following the convention previously employed, the ferrous ion concentration is S; the bicarbonate ion concentration is $2S$, since the solubility of $FeCO_3$ as such is negligibly small. The ionization of carbonic acid is slight, and in the presence of dissolved ferrous bicarbonate, which is highly ionized, may be neglected entirely in the calculation. Table 98 shows the results of experiments at 30°, where the equilibrium constant is

$$K = \frac{S(2S)^2}{(H_2CO_3)}.$$

TABLE 98.—SOLUBILITY OF FERROUS CARBONATE IN CARBONATED WATER

Total concentrations at 30°		Equilibrium constant K
H_2CO_3	$Fe(HCO_3)_2$	
0.196	0.00256	34.2×10^{-8}
0.230	0.00274	35.6
0.309	0.00304	36.5
0.326	0.00311	37.0
0.401	0.00332	36.5
0.655	0.00402	39.8
0.755	0.00434	43.3

The equilibrium "constant" is seen to increase at the higher concentrations, which is in accord with the behavior of most mass-action expressions involving ionized solutes. The pressure necessary to produce a concentration of carbonic acid such as that in the last line of the table is about 25 atmospheres.

It is interesting to note the various other equilibria which also exist in this system, for when a system is in equilibrium it must

[1] H. J. SMITH, *J. Am. Chem. Soc.*, **40**, 879 (1918).

be so as regards all of its parts. Here the solution is saturated with the slightly soluble ferrous carbonate, and the solubility product for this substance must, therefore, be maintained. Since there are carbonate and bicarbonate ions in the presence of carbonic acid, the dissociation relations required of this substance by the mass law must also be maintained. These various equilibria may be expressed by the following chemical equations and their corresponding mass-action expressions:

$$H_2CO_3 = H^+ + HCO_3^- \qquad K_1 = (H^+)(HCO_3^-)/(H_2CO_3).$$
$$HCO_3^- = H^+ + CO_3^{--} \qquad K_2 = (H^+)(CO_3^{--})/(HCO_3^-).$$
$$FeCO_3 \text{ (solid)} = Fe^{++} + CO_3^{--} \qquad K_3 = (Fe^{++})(CO_3^{--}).$$

If now we multiply together the equations for K_1 and K_3 and divide this product by K_2 we have

$$\frac{(Fe^{++})(HCO_3^-)^2}{(H_2CO_3)} = \frac{K_1K_3}{K_2} = K,$$

which is seen to be the equilibrium constant first written for this reaction. K is known from experiment, the dissociation constants K_1 and K_2 for carbonic acid at 30° are 3.7×10^{-7} and 4.9×10^{-11} respectively, whence the solubility product for ferrous carbonate is 45×10^{-12}. The solubility in pure water, in mols per liter, is the square root of this number, or 6.7×10^{-6}. This solubility product was, of course, derived from experiments in the presence of excess carbonic acid, and there was on that account no hydrolysis of the ferrous carbonate. The solubility of 6.7×10^{-6} mols per liter holds only under the assumption for which it was derived, namely, in the absence of any hydrolysis.

The above example is typical of a simple investigation of chemical equilibrium, and illustrates the way in which various equilibrium constants may be combined to give the desired constant governing the equilibrium under consideration.

Conversion of One Solid into Another.—A familiar example of this type of reaction is the conversion of barium sulfate into barium carbonate by boiling it with sodium carbonate solution in excess. The chemical equation is

$$BaSO_4 \text{ (solid)} + Na_2CO_3 = BaCO_3 \text{ (solid)} + Na_2SO_4,$$

and the corresponding mass-action expression is written

$$(SO_4^{--})/(CO_3^{--}) = K.$$

Since the solution is saturated with both solids, the solubility

product for each must be satisfied, *i.e.*, $(Ba^{++})(SO_4^{--}) = k_1$ and $(Ba^{++})(CO_3^{--}) = k_2$. When pure water is saturated with $BaSO_4$, the concentration of each ion is S_1 and k_1 is S_1^2; similarly, k_2 for $BaCO_3$ is S_2^2. These values are

$$(Ba^{++})(CO_3^{--}) = 25 \times 10^{-10} \text{ and } (Ba^{++})(SO_4^{--}) = 10^{-10}$$

for 20°, and upon dividing the second of these by the first we obtain a value for the equilibrium constant K,

$$\frac{(SO_4^{--})}{(CO_3^{--})} = \frac{S_1^2}{S_2^2} = \frac{1}{25} = 0.04.$$

In any solution in equilibrium with both barium sulfate and barium carbonate, the carbonate ion concentration must be 25 times the sulfate ion concentration. Therefore, for the complete conversion of a formula weight of barium sulfate to barium carbonate there will be required a formula weight of sodium carbonate for the chemical reaction, and 25 formula weights of sodium carbonate to maintain the equilibrium ratio or 26 formula weights in all. (This statement does not, of course, apply to a carbonate *fusion* of barium sulfate, for there the sodium carbonate is the solvent as well as the solute; but it does apply to aqueous solutions.) This calculation has been made for 20°, but no smaller quantity of sodium carbonate could be used in a boiling solution safely, since the solution is cooled while filtering.

Suppose 2.33 grams (0.01 formula weight) of barium sulfate is shaken a long time with 100 c.c. of 1 formal sodium carbonate solution, which contains 0.1 formula weight of sodium carbonate. Let x be the mols of sodium carbonate remaining in solution at equilibrium; then $(0.1 - x)$ mols of sodium sulfate are in solution, and $(0.1 - x)/x = 0.04$, whence $x = 0.0962$ mol of sodium carbonate remaining. Then 0.0038 mol of sodium carbonate has reacted, forming 0.0038 mol of barium carbonate, and leaving 0.0062 mol or about two-thirds of the original barium sulfate unchanged. It is clear that too little carbonate solution has been used. As stated above, the minimum quantity required is 26 times the mols of barium sulfate to be converted to carbonate, or 260 c.c. of formal sodium carbonate solution. Any quantity of this solution greater than 260 c.c. will, therefore, convert the sulfate completely to carbonate. Experiments of this kind may be used to determined the solubility product of

one salt when that of another is known, since the equilibrium constant is the ratio of the two solubility products.

Silver reacts with ferric salts, forming ferrous salts and silver salts. The reaction is

$$\text{Ag (solid)} + \text{Fe(NO}_3\text{)}_3 = \text{AgNO}_3 + \text{Fe(NO}_3\text{)}_2,$$

and the equilibrium expression is[1]

$$\frac{(\text{Ag}^+)(\text{Fe}^{++})}{(\text{Fe}^{+++})} = K = 0.128 \text{ at } 25°.$$

From this value of K it may be seen that unless the silver ion concentration is very small, complete reduction of ferric nitrate to ferrous nitrate will not take place. For example, suppose 0.2 formal ferric nitrate to be shaken with an excess of silver until equilibrium is reached. If x is the ferrous ion concentration, $(0.2 - x)$ is the ferric ion concentration, and x is the silver ion concentration, since the chemical equation shows that a silver ion is formed for each ferrous ion. Substituting in the above expression, we have $x^2/(0.2 - x) = 0.128$, whence x is 0.108, the concentration of ferrous salt, and the ferric salt concentration is 0.092. This shows that about half of the ferric salt has been reduced by silver. If some salt is added which precipitates silver ions as soon as formed, and which does not react with the iron salts, then in the presence of solid silver the ferric salt concentration must be very small compared to the ferrous salt concentration, or, in other words, reduction is substantially complete. Addition of a thiocyanate serves this purpose,[2] and by this means ferric iron may be reduced for titration, the thiocyanate furnishing at the same time an indicator for complete reduction. The excess thiocyanate is removed by adding silver nitrate solution just before the titration.

Another reaction of this type is that between lead perchlorate and metallic tin,[3] according to the equation

$$\text{Sn (solid)} + \text{Pb(ClO}_4\text{)}_2 = \text{Sn(ClO}_4\text{)}_2 + \text{Pb (solid)}$$

for which $K = (\text{Sn}^{++})/(\text{Pb}^{++})$. The experimental results for 25° are as follows:

[1] Noyes and Brann, *J. Am. Chem. Soc.*, **34**, 1016 (1912).
[2] Edgar and Kemp, *J. Am. Chem. Soc.*, **40**, 777 (1918).
[3] Noyes and Toabe, *J. Am. Chem. Soc.*, **39**, 1537 (1917).

TABLE 99.—EQUILIBRIUM BETWEEN TIN AND LEAD PERCHLORATE

Molal concentration of solution at start of experiment		Equilibrium concentrations mols per liter		$K = \frac{(Sn^{++})}{(Pb^{++})}$
Tin perchlorate	Lead perchlorate	Sn^{++}	Pb^{++}	
0.094	.....	0.0704	0.0233	3.02
0.050	.....	0.0393	0.0123	3.19
0.050	.....	0.0413	0.0132	3.14
.....	0.096	0.0716	0.0237	3.04
.....	0.060	0.0457	0.0148	3.08
.....	0.050	0.0369	0.0119	3.11
0.038	0.019	0.0428	0.0145	2.96
0.051	0.037	0.0697	0.0239	2.92
0.066	0.027	0.0692	0.0235	2.95
0.086	0.024	0.0821	0.0275	2.98

In some of the experiments the original solution contained lead perchlorate alone, or tin perchlorate alone; in other cases both perchlorates were present in solution; excess of both solid metals was always used and the solutions were shaken at 25° until they had reached equilibrium. As shown by the value of K in the last column of the table, the ratio of tin salt to lead salt in solution at equilibrium is about 3.0, whether the reaction proceeded in one direction or the other, and regardless of the relative quantities of tin perchlorate and lead perchlorate in solution at the start of an experiment. This is a strong confirmation of the principles involved in equilibrium formulations.

It is necessary that the solid phases present be those written in the equation, however. The equilibrium ratio does not apply unless both solids are present, and quite another constant may be obtained if some solid forms which is not shown by the chemical equation.

Thus, if we should formulate the equilibrium expression for the reaction

$$CaSO_4 \text{ (solid)} + Na_2CO_3 = CaCO_3 \text{ (solid)} + Na_2SO_4$$

in the usual way, the equilibrium expression is

$$\frac{(SO_4^{--})}{(CO_3^{--})} = K = \frac{S_1^2}{S_2^2} = \frac{2.3 \times 10^{-4}}{3 \times 10^{-9}} = 7 \times 10^4$$

from which the sulfate ion concentration at equilibrium should

be 70,000 times the carbonate ion concentration. Direct experiment[1] gives quite another value, however, since at equilibrium the solid phases present are not calcium carbonate and calcium sulfate. Solid gaylussite, of the composition $CaCO_3.Na_2CO_3.5H_2O$, forms, and therefore the equilibrium ratio does not conform to that formulated above on an incorrect assumption as to the nature of the solids present. According to experiment, the ratio of sulfate to carbonate is 19 in these solutions. But when the solids present are those shown by the chemical equation, substantial agreement is obtained between calculated concentration ratios and those based on experiments.

Phase Equilibrium.—Before discussing this topic in detail it will be convenient to define two or three new terms, and to repeat the definitions of some other terms previously used.

A *System* is any combination of matter on which we choose to focus attention. For our own convenience we consider a restricted system and study the effect of varying one or another of the external conditions which govern its behavior; the container and any other objects in contact with the system are considered as "surroundings."

The *Phases* of a system are its homogeneous parts which are separated from one another by definite physical boundaries. A gaseous mixture is a single phase, as is a liquid solution or solid solution, but two mutually saturated liquid layers, such as ether and water, constitute two phases. Each pure solid substance is a separate phase, and a mixture of rhombic and monoclinic sulfur would be considered as two phases.

The *Components* of a system are the chemical substances required to make each of its phases in whatever quantity they may be present. Thus one substance, water, is capable of forming all of the phases of the water system; but if the system under consideration is a solution, water and the salt are its components. The number of components is taken as the smallest number of chemical substances capable of forming all of the parts of the system in whatever proportion they may exist. For example, one system composed of calcium oxide, calcium carbonate, and carbon dioxide may be made from a single substance, calcium carbonate. But it is possible for these three phases to

[1] Herz, *Z. anorg. Chem.*, **71**, 206 (1911).

exist together when the amount of calcium oxide is not chemically equivalent to the carbon dioxide present. Since all three substances may be formed in any desired quantity from calcium oxide and carbon dioxide, these two substances may be called the components of the system. It would serve equally well to designate the components as calcium oxide and calcium carbonate, for by adding or removing these two substances any desired quantity of each phase could be brought into a system. This is then a two-component system.

The *Degree of Freedom* of a system, also called the *Variance* of it, is the number of external conditions which may be arbitrarily fixed; the only conditions commonly considered are the composition, temperature, and pressure of the system as a whole.

Phase Diagrams[1] (**Pressure-temperature Diagrams**).—Many pure substances form, in addition to a vapor and a liquid, two or more solid phases. These solids are of different crystalline form, solubility, and physical properties, but they have the same chemical composition. "Grey" tin and "white" tin, rhombic and monoclinic sulfur, red phosphorous and white phosphorus, are familiar from previous chemical study; the several modifications of ice and urethane produced under high pressure are perhaps less well known. Diagrams showing the temperature and pressure corresponding to the existence of various single phases, pairs of phases, etc. are commonly called phase diagrams. Any single phase in a system composed of only one chemical substance may exist throughout a certain temperature range and under a variety of pressures; two phases coexist at a certain definite pressure for each temperature, and cannot exist at any other pressure at this temperature; when three phases are present at equilibrium in a system of one chemical substance, neither the temperature or pressure can be varied. For example, liquid water may exist under any pressure greater than its vapor pressure, and any temperature above the freezing point and below the boiling point corresponding to the pressure imposed, but liquid water and water vapor exist together at any chosen temperature only under the vapor pressure. If at 100° the external pressure

[1] Many other phase diagrams will be found on pages 611–697 of Landolt-Börnstein's Tables; and in HALL and WILLIAMS' "The Examination of Iron, Steel, and Brass."

is maintained at less than 1 atmosphere, no liquid water condenses; if the pressure is made greater than 1 atmosphere, all of the vapor condenses. Only when the pressure is exactly 1 atmosphere can both liquid water and water vapor exist at 100°. Under these conditions, however, the two phases can exist at equilibrium in any relative quantities whatever—a drop of liquid in contact with a large volume of vapor, or a single bubble of vapor in equilibrium with a large quantity of liquid.

Only at the freezing point and under the vapor pressure of ice can all three phases exist. Thus the presence of three phases in a system of one component fixes both the temperature and the pressure. This is, therefore, an invariant system. A two-phase system of one component may exist at one particular pressure for each temperature, or at one particular temperature for each chosen pressure. Since one condition (pressure or temperature) of such a system may be arbitrarily fixed, it is a univariant system. A general relation between the number of phases, the number of components, and the variance of a system at equilibrium will be taken up in a later section.

A simple diagram describing the phases of water is shown in Fig. 52. The line *BDE* is a vapor pressure line, *i.e.*, a line showing the pressure at which liquid and vapor may exist at equilibrium for every temperature. At 60° the vapor pressure is 0.196 atmosphere; accordingly, if water at 60° is acted upon by a greater pressure, all of it remains as liquid; if the pressure is reduced below 0.196, liquid vaporizes until the equilibrium pressure is reached or until all of the liquid is exhausted. At a lower pressure than 0.196 atmosphere the system composed of water at 60° consists of vapor only. Hence the line *BDE* is a two-phase line, defining the pressure at which two phases coexist for each temperature on the diagram. The temperature at which ice and liquid water exist in equilibrium under a pressure of 1 atmosphere is defined as 0° on the Centigrade scale; but since the vapor pressure of ice at 0° is only 0.006 atmosphere, this is not the temperature at which all three phases exist. As calculated on page 99 the melting point of ice is lowered 0.0076° for each atmosphere increase of pressure; hence at 0.006 atmosphere the equilibrium temperature is essentially +0.0076°, and this is the three-phase temperature or triple point. The pressure

at the triple point is 0.006 atmosphere, which is the vapor pressure of both ice and water at 0.0076°, since they are in equilibrium with each other at this temperature. The slight effect of pressure upon the melting point of ice (*i.e.*, the equilibrium between solid and liquid) is shown by the slope of the line *BC* of Fig. 52 to the left.

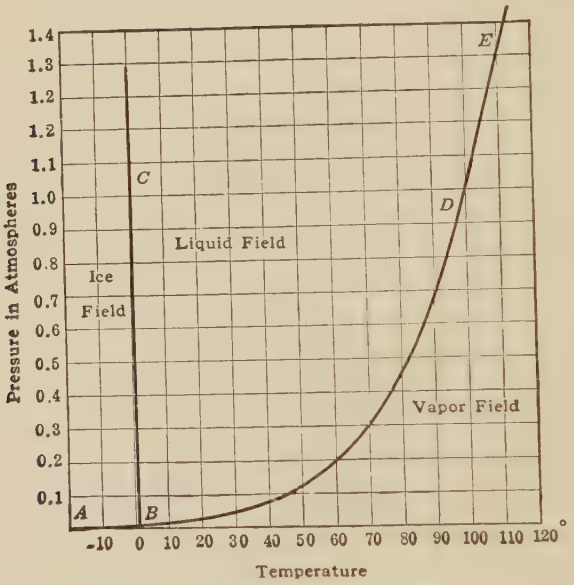


FIG. 52.—Phase diagram for water.

A consideration of the phases of urethane ($CO.NH_2OC_2H_5$)[1] will further illustrate phase diagrams for a system of one component. It forms a vapor, a liquid, and three different solid phases, which we may designate by I, II, and III. As urethane boils at 180°, the vapor field would occupy only a very small area at the bottom of the diagram, corresponding to vapor pressures of less than 1 atmosphere for the temperature range shown. The position of this vapor field is indicated in Fig. 53, showing the pressures and temperatures at which each of the other phases exists.

[1] BRIDGMAN, *Proc. Amer. Acad. Arts Sci.*, **52**, 57 (1916); *Proc. Nat. Acad. Sci.*, **1**, 513 (1915).

Between 52 and 70° equilibrium between liquid and solid I is shown by the line *ab*. It will be noted that this line slopes in the opposite direction to the liquid-solid line for water, indicating that an increase of pressure raises the melting point. As increase

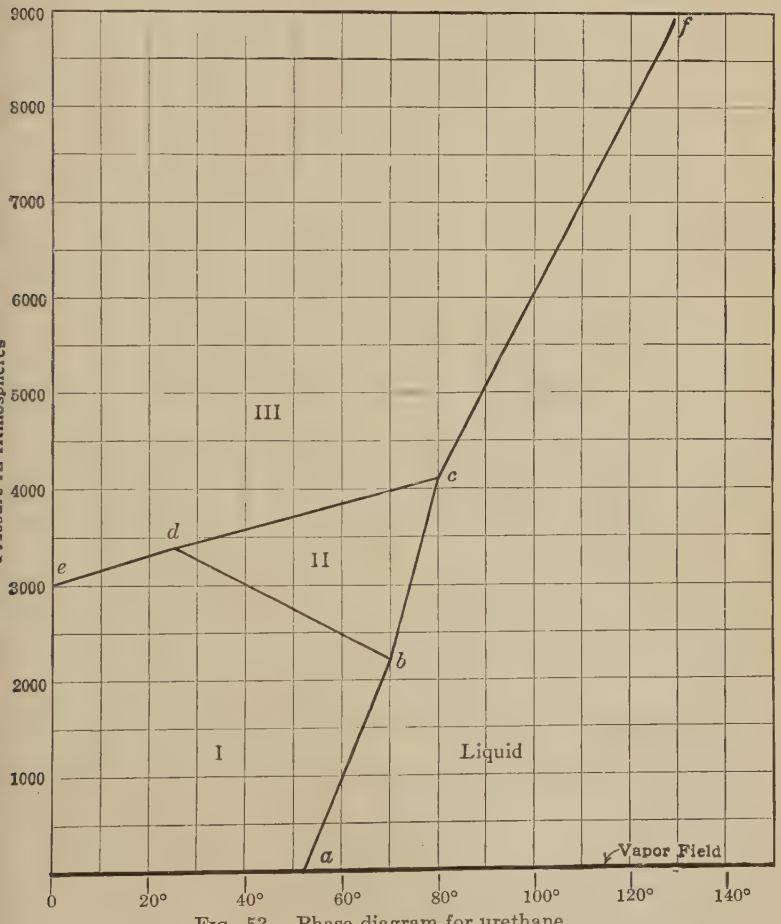


FIG. 53.—Phase diagram for urethane.

of pressure always results in the formation of a more dense substance; solid I is more dense than liquid, and will sink in it. At 70° and 2200 atmospheres (*b*) there is a change in the character of the solid phase, and during transition from I to II there are

three phases present. This is, therefore, an invariant point, and neither temperature nor pressure can change until some phase disappears. Which one will be exhausted first depends upon the conditions of experiment. If heat is added to the system, and such a pressure is maintained that liquid is always present, phase I disappears, and the equilibrium between II and liquid is shown by the line *bc*. The point *c* corresponds to another triple point involving the liquid phase; point *d* is the triple point of all three solids. From experimental determinations of the pressure and temperature of these three triple points, together with the transition pressure of I to III at 0°, the melting point of I at 1 atmosphere, and the melting point of III at 9000 atmospheres, the diagram of Fig. 53 has been constructed. Point *a* is 52° and 1 atmosphere, *b* is 70° and 2200 atmospheres, *c* is 80° and 4100 atmospheres, *d* is 25° and 3400 atmospheres, *e* is 0° and 3000 atmospheres, *f* is 130° and 9000 atmospheres.

Suppose a quantity of urethane to be kept at 60° while (through the steady motion of a piston in a cylinder containing it) its volume is slowly decreased. As the melting point is 52°, the system consists of a liquid at the start; a one-phase, one-component system may exist under various temperatures and pressures, but we have fixed arbitrarily upon a temperature of 60°. The system remains liquid as the volume of it decreases until a pressure of about 900 atmospheres is reached, that is, a point on the line *ab*. Here phase I appears, and until all of the liquid is changed to it we have a two-phase system at a fixed temperature. Hence the pressure will remain constant while the volume decreases to that of the solid alone. As heat is evolved during the solidification, it must be removed from the system in order to keep it at 60°. Finally, all of the liquid changes to solid I, and a further movement by the piston causes an increase of pressure in the system. When a pressure of 2500 atmospheres is reached (line *bd*), I changes to II at a constant temperature and pressure, with a further decrease in volume. Then II is compressed until the pressure reaches about 3800 atmospheres (line *dc*), where it changes to III. Further decrease in volume does not cause the appearance of any new phases.

Let us consider another case, a steady heating under constant pressure. When this takes place under a pressure of 1 atmos-

phere, melting occurs at 52°, vaporization at 180°, and no other phases are formed. Suppose we start with urethane at 0° and a pressure of 3200 atmospheres. Reference to Fig. 53 will show that the system is solid III under these conditions. If the pressure is maintained at 3200 atmospheres by suitable motion of the piston confining it, and heat is added slowly, no phase change occurs until about 10°. Here heat will be absorbed while solid III is changed at a constant temperature to solid I. It will be noted that absorption of heat at this point (on the line *ed*) does not cause a rise of temperature but causes the transition of III to I. As is always the case, a phase stable at high temperatures is formed from one stable at a lower temperature with the absorption of heat. During transition both phases are present at a fixed pressure; hence the temperature cannot change until one phase is exhausted. When all of III has changed to I, further addition of heat raises the temperature steadily until about 30°, where I changes to II with the absorption of heat, in the manner just explained. Phase II is stable at 3200 atmospheres from 30 to 75°, where it melts with the absorption of heat, as in the case of all melting solids.

Heat Effects of Phase Changes.—The Clausius-Clapeyron equation can be used to calculate the heat absorbed during any of these phase changes, when the change of the transition point with pressure is known, or when it can be read off from the slope of a line on a phase diagram. If Δv is the increase in volume attending transition of a gram of substance from one phase to another at the temperature T, and if dp/dT is the change in transition pressure in atmospheres per degree, the heat quantity ΔH will be in cubic-centimeter-atmospheres absorbed per gram. These units may be converted to calories by dividing by 41.2.

Gibbs' Phase Rule.[1]—Denoting by P the number of phases in a system, by C the number of components, and by V the variance, Gibbs' rule is expressed by the equation

$$P + V = C + 2.$$

This is a law limiting the number of phases which may exist together at equilibrium in a system. It tells nothing whatever

[1] For a full discussion of this equation see "The Phase Rule and Its Applications" by ALEXANDER FINDLAY (1923).

as to *what* phases exist, but only the maximum number which may exist under specified conditions. Let us consider the system CaO, CO_2, $CaCO_3$, which is a two-component system, since the third phase may be made from the first two. When all three phases exist, application of Gibbs' equation shows that $V = 1$. This means that all three phases may exist in equilibrium at different temperatures, provided the pressure is not specified, or at different pressures, provided the temperature is not specified. Since $V = 1$, either pressure or temperature may be specified, but not both. Even this freedom is only within certain limits, imposed by the chemical properties of the system. Thus we may not specify that a system composed of only these substances shall exist at 4000°C., for at that temperature carbon dioxide dissociates into carbon monoxide and oxygen to a certain extent, and there are other chemical substances present which were not present in appreciable quantity at lower temperatures. But suppose we say that all three phases of this system shall exist at 900°, we must adjust the pressure to the dissociation pressure of calcium carbonate at 900° (760 mm.); if we have this three-phase system at 800°, the pressure must be the dissociation pressure corresponding to this temperature (180 mm.). Of course, we might have specified the pressure of 760 mm., and sought the temperature at which this dissociation pressure exists.

Suppose we specify that this system shall be brought to 600° and 1 atmosphere, we have taken $V = 2$; application of the equation to determine the number of phases existing under these conditions shows that $P = 2$. Hence some two phases of this system can exist together at this temperature and pressure, but the phase rule says nothing as to what the phases are. They may be calcium oxide and calcium carbonate, carbon dioxide and calcium carbonate, but not calcium oxide and carbon dioxide, for the specified pressure is greater than the dissociation pressure of calcium carbonate at this temperature. It should be further noted that the phase rule gives only the *maximum* number of phases, and that it does not state that one phase may not exist alone at a specified temperature; only that there shall not be more than two phases.

Temperature-composition Diagrams.—Most experimental work is carried out under a pressure of 1 atmosphere. It is

convenient and instructive to show by diagrams the conditions of equilibrium in two-component systems of varying composition at different temperatures, when the pressure is maintained constant. While these diagrams are sometimes called phase-rule diagrams, they are not properly mere applications of the phase rule. This rule is qualitative only; the diagrams show quantitatively the conditions of equilibrium in a system. We shall consider only two-component systems. In these diagrams the abscissæ show the composition of the *system as a whole*, ordinates show temperature variations. Certain vertical lines in the diagrams therefore correspond to the composition of some particular phase of the system. Solubility curves are familiar examples of such diagrams, as are also curves showing the freezing point of a solution as a function of the composition. Such diagrams are of prime importance in the study of alloys, which are usually solutions of metals in metals, and which often form metallic compounds. Let us consider first a simple freezing-point-composition diagram for a two component system.

System: Lithium Chloride and Potassium Chloride.—Fused potassium chloride dissolves lithium chloride, which thereby lowers the freezing point of the solution, *i.e.*, the temperature at which the liquid is in equilibrium with solid potassium chloride. The data are as follows:

Mol per cent of lithium chloride	0	34.3	39.5	42.6	55.8	58.5
Freezing point, degrees	773	600	552	527	385	361

But potassium chloride is soluble in fused lithium chloride also, and it lowers the freezing point of lithium chloride. The following are the experimental results:

Mol per cent lithium chloride	100	64.4	59.4	58.5
Freezing point, degrees	601	412	372	361

When the mol per cent of lithium chloride in solution is 58.5, the liquid is in equilibrium with both solid KCl and solid LiCl at 361°; this is called the eutectic point. Upon plotting these figures in a diagram in which the mol fraction of lithium chloride *in the system* is shown as abscissæ, Fig. 54 results.[1] The field

[1] RICHARDS and MELDRUM, *J. Am. Chem. Soc.*, **39**, 1816 (1917). Similar diagrams are obtained for systems composed of AgCl and KCl, $BaCl_2$ and $CaCl_2$, AgCl and RbCl.

above *abcde* is the liquid field; systems of any composition consist of liquid solution of one salt in the other at all points above this line. Let us study the behavior of a solution in which the mol fraction of lithium chloride is 0.35 when it is cooled from 700 to 300°, the path of which process is indicated by the dot-and-dash line on the figure. At 700° the system under a pressure of 1 atmosphere consists of solution alone, and it remains liquid until about 600° (point *b* on the diagram).

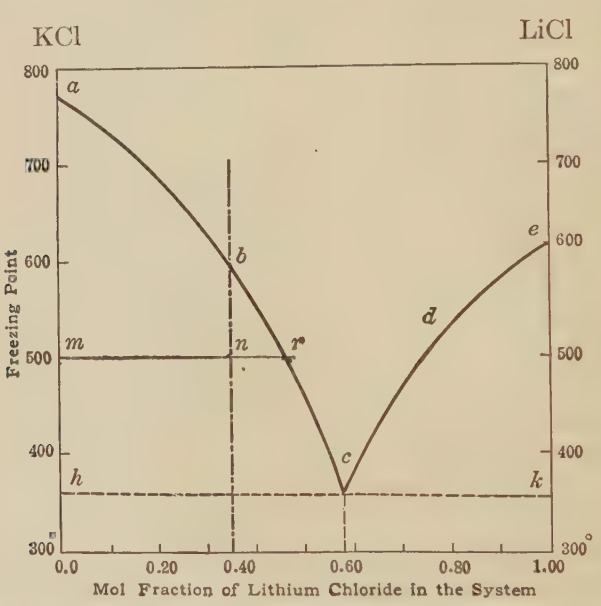


FIG. 54.—Phase diagram for lithium chloride in potassium chloride.

At this temperature solid potassium chloride begins to separate from the melt. The composition *of the system* remains constant, but a new phase appears whose composition is shown by the left-hand margin (*i.e.*, pure potassium chloride); and owing to the separation of pure potassium chloride from the melt, the mol fraction of lithium chloride in the melt increases; at 500° considerable solid potassium chloride will have separated out, and the mol fraction of lithium chloride in the melt is about 0.45. If heat has been withdrawn from the system at a uniform rate of so many calories per minute, the fall of temperature will take

place more slowly after reaching *b*, owing to the heat evolved when potassium chloride solidifies. As the cooling proceeds, more solid separates, and the composition of the melt is shown for each temperature by the line *bc*, until at 361° the liquid is saturated with both potassium chloride and lithium chloride; both salts separate at this point, and the temperature remains constant until all liquid disappears. As this is a three-phase point at a specified pressure, no further variance is possible in the light of the phase rule.

Let us return to a consideration of the system at 500°, which is at the point *n* in the field *ahc*. The system contains 0.35 mol of lithium chloride to 0.65 of potassium chloride, but one phase of the system is pure potassium chloride; hence the other phase must be poorer than the system as a whole in this component. There is another fact to be derived from the dimensions of the diagram, namely, that the relative quantities of solid potassium chloride and of solution at 500° are to each other as the lengths *nr* and *nm*. At *b* the length corresponding to *nr* is zero, which means that no solid potassium chloride has separated yet; at 400° the length of *nr* is longer in proportion to that of *mn*, corresponding to a further separation of potassium chloride as the temperature is lowered.

We may also designate the phases existing in a system whose composition *as a whole* is shown by the abscissæ at any temperature. In the field above *abcde* such a system is liquid only; in the field *ahc* it consists of solid potassium chloride in equilibrium with solutions of varying composition. The composition of the solution saturated with potassium chloride for each temperature is shown by the line *abc*. In *cke* the phases of the system are solid lithium chloride and a solution which is saturated with this solid and which changes its composition with changing temperature along the line *cde*. Below the line *hck* a mixture of the two solid salts exists. This diagram is typical of all two-component systems if the substances mix in all proportions in the liquid state, and provided they do not form a compound; it is the simplest type of such diagrams.

The Eutectic Mixture.—A mixture of two solids, such as that which separates at 361°, is usually referred to as "the eutectic," but it should be clearly understood that it is a mixture of

two separate phases. There is no such thing as the "eutectic phase." When a liquid is cooled, the component which first separates appears in larger crystals than those forming at the eutectic temperature. There both solid phases separate in an intimate mixture which is of finer grains than the crystals of single component already separated, but this may be seen under a microscope to consist of separate crystals of each substance. The phases of the eutectic are only those which separate at temperatures above the eutectic temperature, as indicated by the two intersecting curves. The eutectic mixture is that inti-

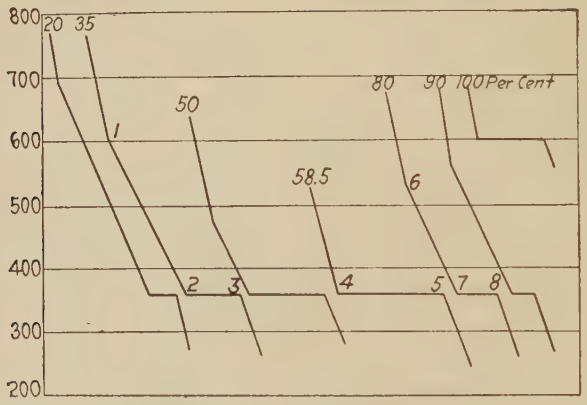


FIG. 56.—Cooling curves for the system shown in Fig. 54.

mate mixture of *two phases* separating at the constant temperature which marks the lower limit for the existence of liquid.

Cooling Curves.—If the temperature of a system undergoing cooling at a uniform rate is measured every minute, and a diagram is drawn showing these temperatures against time as abscissæ, abrupt changes in slope indicate the processes occurring during cooling. A group of such curves for a series of mixtures of KCl and LiCl is shown in Fig. 56.

In cooling a mixture in which the mol fraction of LiCl is 0.35 from 700 to 600° there is no process occurring in the system which evolves heat except the cooling process. At 600° solid potassium chloride begins to separate, giving rise to more heat, and hence the rate at which the temperature falls is slower, though heat is being withdrawn from the system at a constant rate. There will,

therefore, be a break in the slope of the curve at this point (1 in Fig. 56). At 361°, where both solids are separating, since this is a three-phase condition in a two-component system under a specified pressure, the temperature remains constant (2, 3) even though heat is being taken from the system; the heat evolved is the latent heat of solidification of the component salts. The fourth line of Fig. 56 is a cooling curve for a solution of composition 0.585, which deposits both solids at 361°; the next line shows a cooling curve for a solution containing 80 mol per cent of lithium chloride. At the point 6 (520°) solid lithium chloride begins to separate, and the composition of the melt changes along the line *edc* of Fig. 54 as the temperature falls; at point 7 (361°) both solids separate, as in cooling the other solutions. For pure lithium chloride the cooling curve would have the same form as the 58.5 per cent curve, with the horizontal portion at 601°, the melting point of the pure salt.

Thermal Analysis.—In any given piece of apparatus a constant rate of heat loss can be maintained, and the time interval during

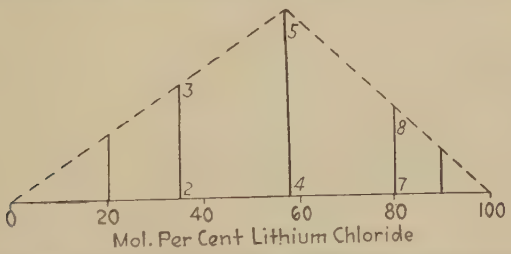


FIG. 57.—Showing the time required for solidification at the eutectic temperature.

which eutectic mixture is separating is proportional to the weight of it formed. In other words, the quantities of eutectic mixture are proportional to the lengths of the horizontal portions of curves like those in Fig. 56. If, therefore, portions of curves for the rate of cooling of a fixed quantity of the various mixtures—such as the portions 2, 3; 4, 5; and 7, 8 of the curves of Fig. 56—are plotted vertically against the composition of the system as a whole, a triangle is obtained, as shown in Fig. 57. This is to be expected, since a solution of the same composition as the eutectic solidifies entirely at one temperature. From this

plot it is possible to make a rough analysis of an unknown mixture of the two components by determining the length of time required to solidify all of its eutectic in the standard apparatus. Knowing then the weight of system taken, we may estimate from the weight of eutectic the percentage of each component. It is necessary to determine in some other way whether the given sample lies on the right- or left-hand side of the eutectic, but this is usually known, or may be estimated from specific gravity or some other easily determined property.

Two-component System in Which a Compound Forms.—If the two components of a system mix in all proportions in the liquid state, but form a solid compound, a diagram of somewhat different character shows the phase equilibrium. Each component dissolves in the compound to lower its freezing point, and the compound dissolves in each pure component to lower its freezing point. Let us build up such a diagram from the corresponding cooling curves for the system magnesium and tin described in Table 100. It will be seen that a compound is formed which contains 71 per cent of tin by weight, or 71/119 = 0.59 atomic

TABLE 100.—SYSTEM MAGNESIUM AND TIN

Weight per cent of tin in the system	0	20	30	50	60	71	80	90	97	100
First break in cooling curve	650°	610°	585°	675°	750°	785°	700°	400°	210°	232°
Horizontal portion of cooling curve	650°	565°	565°	565°	565°	785°	210°	210°	210°	232°

weight of tin to 29/24.3 = 1.18 of magnesium; that is $SnMg_2$, and that it melts at 785°. Further, the eutectic formed of pure tin and compound solidifies at 210° and that composed of compound and magnesium solidifies at 565°. Our diagram will consist of two portions, each similar to Fig. 54. The composition of the second eutectic is shown by the 97 per cent solution solidifying all at one temperature; that of the other eutectic is not given, but may be obtained as shown below. Inserting the known points on a diagram and connecting with lines, we obtain the diagram of Fig. 58, and by extending the freezing curves smoothly, the first eutectic is seen to contain about 35 per cent of tin. The left-hand 71 per cent of this diagram corresponds to the two-

component system magnesium-Mg_2Sn; the right-hand 29 per cent to a system Mg_2Sn-tin; but it is convenient to cover the whole range of composition on a single sketch. Each portion of this diagram may be treated exactly as was Fig. 54. The relative weights (since the plot shows percentage by weight) of compound and liquid melt in a system consisting of 50 per cent by weight of tin at 600° are to each other as the lengths *nr* and *mn* on this diagram. When the cooling of a system containing 85 per cent of tin is carried out as indicated on Fig. 58 by the dot-and-dash line, compound separates from the melt at 590° and the melt

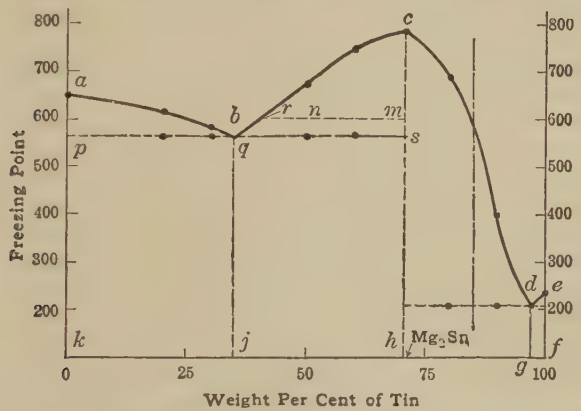


FIG. 58.—Phase diagram for the system magnesium and tin.

changes composition during cooling as shown by the line *cd* until 210° is reached, where both compound and pure tin separate at a constant temperature until all of the liquid phase is exhausted.

Systems which form a compound have, in general, this type of diagram when the solid phases are those indicated, but before applying these considerations to a given system it is first necessary to ascertain that the solid phases are the pure components or are compounds formed from them. As in the case of reactions involving solutions and solids, the equilibrium conditions cannot be represented quantitatively on a diagram unless the exact nature of the solid phase is known.

Solid Solutions.—So far we have considered in connection with freezing points only those cases in which a pure substance separates on cooling. In the case of alloys, and less frequently

in other melts, the solid which deposits is a perfectly homogeneous crystal phase containing both components, but in indefinite proportions, *i.e.*, in other than atomic or molecular ratios. It is not a fine crystalline meal of pure crystals of each component as in the eutectic, but a single crystal containing in its lattice two kinds of atoms. These are sometimes called mixed crystals, more often solid solutions, and, as is the case in liquid solutions, they are of indefinite proportions. Some substances form solid solutions in all proportions, just as some liquids mix in all proportions; others have only limited solubility.

The case of total miscibility is parallel to the partial condensation of a vapor from a liquid mixture, which was considered under fractional distillation. A simple example is the alloy of copper and nickel, for which the "freezing points" are as follows:

Per cent copper	0	25	50	75	100
Apparent "freezing point," degrees	1450	1400	1310	1210	1080

These temperatures might better be called the solidification temperatures, since a freezing point is the temperature at which a solution is in equilibrium with pure solid solvent, and the crystal which separates in this case is a *solid solution*.

A liquid solution containing 25 per cent of copper deposits upon cooling a first crystal containing 10 per cent of copper, the 50 per cent solution deposits a crystal containing 30 per cent, and the 75 per cent solution gives a crystal containing 55 per cent of copper. In each case, these figures refer only to the first small portion of solid deposited. As the temperature falls, the composition of the liquid changes; that of the solid also changes, as in the fractional condensation of vapors. The average composition of the whole alloy after solidification is complete is, of course, the same as that of the liquid melt, but the first portion of solid separating is poorer in copper than the original liquid; the last drop of liquid to solidify is richer in copper than the original melt. The temperature at which deposition of solid begins is shown in Fig. 59 by the solid line; the composition of the solid solution first deposited from each solution is shown by the dotted line. The phase fields may be written upon this diagram, as in other temperature-composition diagrams. Below the dotted line all of the alloys of nickel and copper are solid solutions, above

the solid line all of them are liquids. In the field between these lines, two phases exist. For example, at 1240° a system composed of 60 per cent copper and 40 per cent nickel consists, at equilibrium, of a solid solution containing 50 per cent copper (point *a*) and a liquid solution containing 70 per cent copper (point *b*). If such a system were cooled from 1500 to 1000°, the first crystal deposited would contain about 35 per cent of copper and would appear at about 1275°; the last drop of liquid to solidify would contain about 80 per cent of copper; and solidification would be complete at 1190°.

At the right of Fig. 59 are shown two typical cooling curves for such a system. The portion between the two breaks corresponds to the range in which solid is depositing. As each

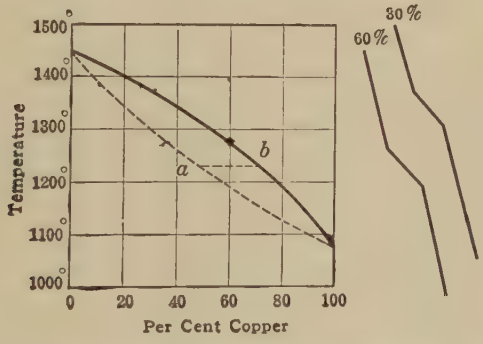


FIG. 59.—Phase diagram for the system copper and nickel.

iquid deposits a solid solution of different composition, there is no horizontal portion in such curves. A solid solution is *one phase*, and a horizontal portion in a cooling curve for a two-component system demands two solid phases and a liquid phase.

Solid Solutions of Incomplete Miscibility.—Alloys of aluminum and zinc do not form solid solutions over the whole range of composition from pure zinc to pure aluminum, and the two metals do not form a compound. Solutions containing less than 5 per cent of aluminum deposit upon cooling pure zinc crystals until the eutectic is reached. The two phases forming the eutectic are pure zinc and a solid solution containing 55 per cent aluminum. This is the *saturated solid solution;* and solutions containing more than 55 per cent of aluminum are not saturated

with zinc. Thus a melt containing 60 per cent of aluminum begins at 540° to deposit a solid solution containing 80 per cent of aluminum; as the temperature continues to fall, the composition of liquid melt changes along the line *ab* of Fig. 60; that of the solid deposited from it changes according to the line *cb*. A 40 per cent melt deposits at 480° a solid solution of about 70 per cent aluminum, and as the temperature is lowered the melt changes its composition along *ab* until the eutectic temperature of 380°, where zinc and the saturated solid solution are deposited. The behavior of these alloys will be made clearer from a careful

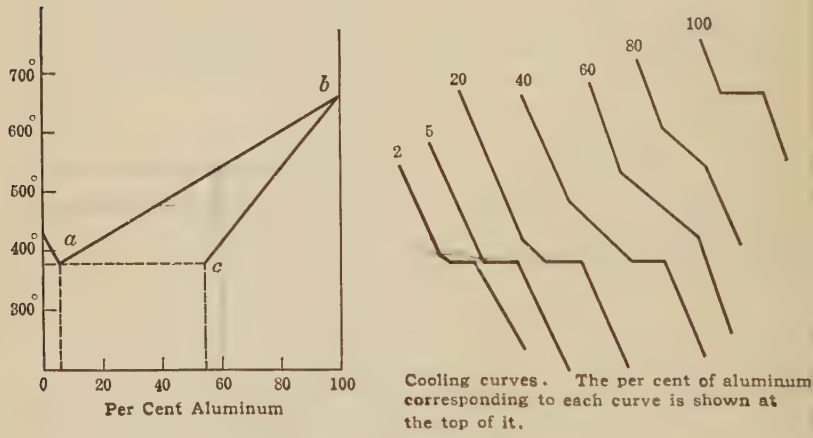


FIG. 60.—Phase diagram for the system aluminum and zinc.

study of the cooling curves of Fig. 60. The student should determine from the phase diagram what phases are in equilibrium along each portion of each curve given, and tabulate these results.

Partially Miscible Liquids.—Aniline and hexane are only partially soluble in one another[1] at room temperatures, but each solubility increases as the temperature is raised and at about 60° the miscibility becomes complete. The temperature 60° is called the critical solubility temperature. If a solution containing 50 per cent of each liquid is cooled, it separates into two layers just below 60°, having the compositions shown by the two branches of the curve of Fig. 61. At 20° one layer consists

[1] D. B. KEYES and HILDEBRAND, *J. Am. Chem. Soc.*, **39**, 2126 (1917).

of about 8 per cent hexane (this is a saturated solution of hexane in aniline) and the other consists of 93 per cent hexane (saturated solution of aniline in hexane). The vapor pressures of the components from each of the phases are greater than those computed from Raoult's law, indicating that the two substances have little attraction for one another as is also shown by the slight solubility.

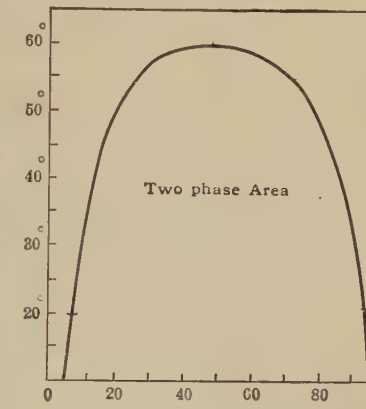


FIG. 61.—Solubility of aniline in hexane.

Within the area under the curved line a system of aniline and hexane having the composition shown on the bottom of Fig. 61 consists of two mutually saturated solutions; as the temperature is raised, each solution takes on some of the "solvent" in the other; that is, the mol fraction of "solute" in each layer increases as shown, until at the critical solubility temperature the liquids mix with each other in all proportions. The temperature of this critical solubility for several other liquid systems which form two layers at room temperature is shown in the table below. In every case the maximum point in the

TABLE 101.—CRITICAL SOLUBILITY TEMPERATURE

System	Critical solubility temperature
Water and nitrobenzene	245
Water and *o*-nitrotoluene	262
Phenol and isopentane	66
Aniline and isopentane	79
Phenol and hexane	43
Phenol and octane	50

solubility curve occurs in the diagram over the point corresponding to about 50 per cent of each component. In these systems the average composition of the two layers is a straight-line

function of the temperature,[1] a fact corresponding to the law of linear average densities for liquid-vapor systems (law of Cailletet and Mathias, page 85). This rule is of use in determining the exact composition corresponding to the critical solubility temperature. These critical solubility temperatures are often far above the boiling points of the components, so that complete solubility is not attained without the application of considerable pressures.

Solubility of the Hydrates of Zinc Nitrate.[2]—The diagram of Fig. 62 represents equilibrium between the phases of a system composed of zinc nitrate and water. The possible solid phases within the temperature and composition range of this diagram are ice, solid $Zn(NO_3)_2.3H_2O$, $Zn(NO_3)_2.6H_2O$, and $Zn(NO_3)_2.9H_2O$; the liquid phase is a solution of zinc nitrate in water, and there is no vapor phase present, since the data refer to a pressure of 1 atmosphere, and none of the constituents has a vapor pressure as large as 1 atmosphere within the temperature range considered. The composition of the *system as a whole* is shown on the bottom of the diagram.

Curve *ab* of the figure represents the freezing-point curve for zinc nitrate solutions whose compositions in per cent by weight of anhydrous zinc nitrate are shown on the bottom axis. The freezing point of each solution may be read off at the left-hand margin. A solution containing 20 per cent zinc nitrate by weight freezes at $-9°$; further cooling of this solution results in depositing more ice, with the formation of a solution containing a larger percentage of zinc nitrate. At $-20°$ the system whose composition as a whole is 20 per cent zinc nitrate (shown at point 1) consists of ice and a solution containing 33 per cent of zinc nitrate. Further cooling of this 20 per cent system causes the solution to increase its concentration along the line *ab*, with the separation of more ice, until at $-29°$ the eutectic temperature is reached, and solid $Zn(NO_3)_2.9H_2O$ appears. This is then a three-phase system under an arbitrary pressure of 1 atmosphere, and since it is a two-component system, three phases make the system invariant. The phase rule is

$$P + V = C + 2;$$

[1] Campetti and Grosso, *Nuovo cimento*, **6**, 379 (1913).

[2] Mylius and Funk, *Wiss. Abhandl. Phys.-Tech. Reichsanstalt*, **3**, 438 (1900).

hence with three phases, the variance, or degree of freedom of the system, is unity, and the arbitrary condition of pressure has already been imposed. Further withdrawal of heat causes the

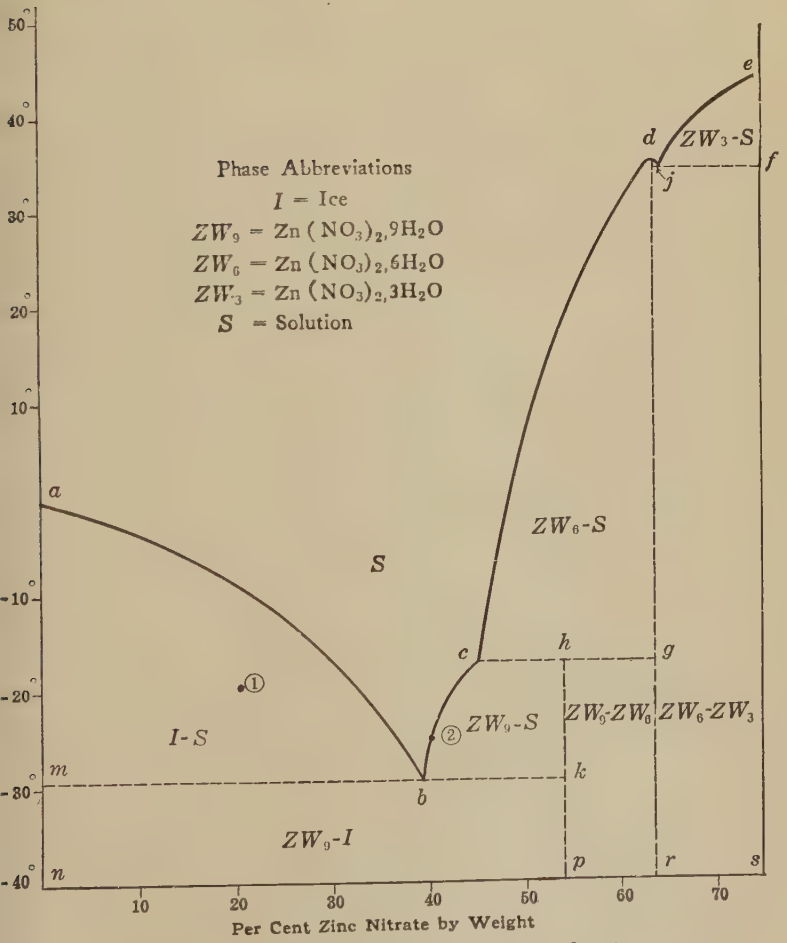


FIG. 62.—Phase diagram for zinc nitrate and water.

solution to deposit ice and solid $Zn(NO_3)_2.9H_2O$ at a constant temperature until all of the solution is exhausted, after which cooling produces no new phases. When any solution of zinc

nitrate containing less than 39 per cent of the salt by weight is cooled, it behaves in this manner, depositing ice at the temperature shown by the line *ab*, and increasing the concentration of the solution until $-29°$ is reached, where the whole system solidifies.

Curve *bc* shows the solubility of $Zn(NO_3)_2.9H_2O$ in water as a function of the temperature. For the sake of brevity, we shall write this hydrate ZW_9 to indicate nine molecules of water to one of zinc nitrate. At $-25°$, if the system as a whole has the composition 40 per cent *Z* (point 2), it consists of solution alone. If the temperature is reduced to $-28°$, ZW_9 separates out, and the system consists of two phases. (It should be made clear that the figures at the bottom of the diagram refer to the composition of the system *as a whole*, and that this is not the composition of any phase of the system unless the whole system consists of a single phase, as it does above or on the line *abcde*, for example.) When this solution is cooled to $-29°$, ice separates, and the system then consists of three phases, ice, ZW_9, and solution. Since the arbitrary condition of atmospheric pressure has been imposed upon the system, this is in the light of the phase rule a non-variant system, and the temperature remains constant while heat is withdrawn from the surroundings until all of the solution is changed to ice and solid ZW_9. The system is then in the field *mkpn*, and further cooling forms no new phases. Any solution containing between 39 and 45 per cent *Z* which is gradually cooled will begin to deposit ZW_9 when the line *bc* is reached, and will continue to deposit this phase until $-29°$ is reached. This is the eutectic temperature, and both ice and ZW_9 are formed until the solution is exhausted. At any point within the field *bkhc*, the system consists of solution in equilibrium with solid ZW_9. Suppose a system of 50 per cent *Z* were heated slowly from $-25°$, it would consist of solid ZW_9 and its saturated solution until $-17°$ is reached. This is the transition temperature of ZW_9 to ZW_6, and hence at this temperature a new phase appears. The system is then an invariant one; heat is absorbed at constant temperature and used to change ZW_9 into ZW_6 until all of the former is exhausted, and the system again consists of only two phases. Further heating causes the solution to increase its concentration as shown by the line *cd* until at $+5°$ all of the solid ZW_6 is dissolved, and a single-phase system results.

From the molecular weights of zinc nitrate and of water it may be computed that ZW_9 contains 53.9 per cent of Z by weight. Suppose pure ZW_9 to be heated from $-40°$ (point p) to $+40°$ by a slow, uniform addition of heat to the system. It remains one phase until $-17°$ is reached (line *chg*), where the solid ZW_9 decomposes into ZW_6 and solution saturated with this hydrate. During decomposition there are three phases present, so the temperature remains constant until all of the ZW_9 has been exhausted. Further heating causes more ZW_6 to dissolve until 20° is reached, when all of it will have passed into solution, and the system above this temperature consists of a single phase.

The hydrate $Zn(NO_3)_2.6H_2O$, or ZW_6, consists of 63.6 per cent by weight anhydrous zinc nitrate. A solution of this composition will exist above 36.5°, but if cooled to this temperature will deposit pure ZW_6; point d therefore is the melting point of ZW_6. Addition of more Z will lower the melting point until point j is reached, which is the eutectic for ZW_6 and ZW_3.

Suppose a solution of 60 per cent Z were cooled at a uniform rate from 50 to $-30°$. By a uniform rate of cooling, a given number of calories per minute are withdrawn from the system; this may or may not produce a uniform fall of temperature, depending on whether phase changes are taking place or not. When 31° is reached, the solution deposits solid ZW_6, and the rate of temperature fall is less than when no solid was separating out. This solid continues to separate out until $-17°$ is reached, which is a point on the line *chg*, and the transition temperature of ZW_6 to ZW_9. At this point ZW_9 forms from ZW_6 and solution until all of the solution is exhausted, when the field *khgr* is entered, and further cooling forms no new phases.

The behavior of this solution differs from that of a 50 per cent solution at $-17°$ in that a 50 per cent solution forms ZW_9 from ZW_6 and solution until all of the ZW_6 is exhausted, when some solution still remains. Further cooling therefore results in further deposition of ZW_9 and a decrease in the quantity of solution, which changes its composition along the line *cb* until point b is reached. Here ice and solid ZW_9 separate until all of the solution is exhausted.

The line *je* shows the solubility of ZW_3, and any system having a composition and temperature to bring it within the

field *fje* consists of solution and pure solid ZW_3. As this solid contains more than 75 per cent anhydrous zinc nitrate, its composition line, corresponding to *hkp* for ZW_9 and *dgr* for ZW_6, does not appear on this diagram.

A solution containing 70 per cent Z when cooled would deposit ZW_3 at 42°, and continue to deposit this phase while the solution changed its composition along *je* until 35°, where the solid hydrates ZW_3 and ZW_6 would both deposit until all of the solution was used up; the field *jfsr* would be entered, and further cooling would lead to the formation of no new phases. Systems such as this one of zinc nitrate and water may be studied by means of cooling curves, just as in the case of alloys. It should be noted that the separation of a phase upon cooling always takes place with the evolution of heat, hence with a decrease in the rate of temperature fall when heat is withdrawn from the system at a uniform rate. When an invariant point is reached, two phases are separating at once, and no change in the temperature of the system is produced by cooling until one of the phases has been exhausted.

Study Question.—Draw cooling curves for systems containing the following percentages of zinc nitrate, and write upon each portion of each curve the phases present; 0, 10, 20, 39, 42, 45, 50, 53.9, 60, 63.6, 70. Plot temperature vertically, time in arbitrary units horizontally, and note that an invariant system evolves heat without changing its temperature, until it ceases to be an invariant system.

Questions

1. From the data of Table 92 calculate the least quantity of hydrogen which will reduce a formula weight of silver sulfide (Ag_2S) to silver at 617°C. Calculate also the weight of silver required to react with a mixture of a mol of hydrogen and one of hydrogen sulfide to produce equilibrium in the presence of both solids at this temperature.

2. Calculate the heat absorbed by reaction between silver and hydrogen sulfide from the equilibrium constants.

3. Ten grams of silver sulfide remain in contact with a liter of hydrogen at 700° until equilibrium is established. (*a*) Calculate the equilibrium constant of the reaction at this temperature from the data given in Table 92. (*b*) Calculate the mol fraction of hydrogen sulfide in the gaseous mixture at equilibrium. (*c*) What is the least quantity of hydrogen which would reduce all of the silver sulfide to silver at this temperature?

4. Describe in detail, by reference to Fig. 53, what would happen if urethane at 35° and 5000 atmospheres were allowed to expand slowly while the temperature remained constant. Do the same for a temperature of 100°.

5. Describe the changes in a system composed of urethane when it is cooled from 100 to 0° under constant pressures of 1 atmosphere, 2500 atmospheres, 3000 atmospheres, 3500 atmospheres.

6. State what phases exist in each of the fields of Fig. 58.

7. State what phases exist in each of the fields of Fig. 60.

8. Metal *A* melts at 500°, *B* melts at 600°, and the compound formed by them, *AB*, melts at 1000°. No solid solutions are formed. Draw a temperature-composition diagram showing in a general way the nature of this system, choosing reasonable points for the location of other characteristic points of the diagram for which data are not given. Draw through this diagram vertical lines at 5, 40, and 90 atomic per cent *A*, and at a minimum point in the diagram, and draw a curve showing the rate at which the temperature would rise through each of these portions of the diagram if heat was added at a uniform rate. These curves are called heating curves; breaks in them may be employed to show the character of any phase changes occurring during heating.

9. Potassium acid sulfate ($KHSO_4$) forms four solid phases and the triple points are as follows:

I–II–IV	199°	1830 atmospheres
II–III–IV	118°	2900 atmospheres

Phase III is stable at room temperatures and pressures, and it changes to IV at about 48° and 6000 atmospheres. The transition points under 1 atmosphere are 164 and 180°, and phases I and IV are in equilibrium at 220° and 2500 atmospheres. (*a*) On a diagram covering the range 40 to 350° and 0 to 6000 atmospheres, draw lines representing the equilibrium between the solid phases, and letter each field to show what phase is stable within it. (*b*) The melting point is 210° and the solid sinks in the liquid. Draw a short line (0 to 200 atmospheres, say) showing the equilibrium between liquid and solid, and show by exaggerating the slope of this line whether the melting point is raised or lowered with increase of pressure. (*c*) Tell in detail all that would happen if $KHSO_4$ were heated very slowly from 40 to 260° under a pressure of 2500 atmospheres, but do not draw any conclusions which are not justified by the data given.

10. Phenol (m.p. 45°) and water form at 20° two liquid phases, one of which contains 8.4 per cent phenol, the other 72 per cent phenol. The two substances are miscible in all proportions at temperatures above 67°. (*a*) Draw a temperature-composition diagram for this system. (*b*) What would happen at 50° on adding successive small portions of phenol to water until the system was 99 per cent phenol? (*c*) What would happen on cooling a 50 per cent phenol solution from 80 to −25°? Describe the texture of the solid system. (*d*) Same as *c* for 1 per cent and for 99 per cent phenol solutions. (Hill and Malisoff, *J. Am. Chem. Soc.*, **48**, 918 (1926).)

11. Bismuth (m.p. 267°) and tellurium (m.p. 426°) form a compound (m.p. 575°) containing 48 per cent of tellurium by weight. No solid solutions form; the two eutectic temperatures are 261 and 388°. Draw a temperature-composition diagram for this system and letter its fields. Draw cooling curves showing the behavior of melts containing 10, 40, 65, and 95 per cent tellurium when cooled from 600 to 200°. Indicate on each curve the phase which appears or disappears at each break in it. What would happen at 400° if tellurium is added gradually to bismuth, assuming equilibrium to be maintained at all times?

12. The system water up to pressures of 5000 atmospheres and below 0° forms four solid phases and one liquid phase. The triple points are as follows for ice I, ice II, ice III, ice V, and liquid:

I–III–liquid	−22°	2100 atmospheres
I–II–III	−35°	2130 atmospheres
III–V–liquid	−17°	3500 atmospheres
II–III–V	−24°	3500 atmospheres

(Ice IV does not appear on the diagram.)

Two phases only are present at −40° and 5000 atmospheres; at −40° and 2000 atmospheres; and at −10° and 5000 atmospheres. Draw a sketch of the pressure-temperature diagram covering the range of 0 to −40° and 0 to 5000 atmospheres. What conditions are represented by the line joining the two triple points at 3500 atmospheres? What is the significance of the straight line joining −22° and 2100 atmospheres to 0° and 1 atmosphere? Will ice V float or sink in the liquid in contact with it?

13. Naphthalene ($C_{10}H_8$) lowers the freezing point of phthalic anhydride ($C_6H_4(CO)_2O$) as follows:

Mol per cent anhydride	0	8.07	15.3	21.7	26.1
Freezing point	80	75.1	71.2	67.3	64.9

and phthalic anhydride lowers the freezing point of naphthalene:

Mol per cent anhydride	100.	90.5	80.7	67.3	44.8	32.2	26.1
Freezing point	130.8	124.8	118.5	109.2	88.9	73.5	64.9

Construct from these data the temperature-composition diagram of the system and letter its fields to show what phases exist within them. No solid solutions form. (Monroe, *J. Ind. Eng. Chem.*, **11,** 1119 (1919).)

14. Toluene-*o*-sulfonamide and the corresponding para-compound mix in the liquid state in all proportions, and each lowers the freezing point of the other as follows:

Per cent para compd	0	17.96	25.87	35.58	40.54	50.39	61.15	82.59	100.
Freezing point	156.3	145.5	139.7	133.6	130.3	120.8	110.4	126.8	137.5

Construct from these data the temperature-composition diagram. (McKie, *J. Chem. Soc. London*, **113,** 799 (1918).)

15. Calculate the heat absorbed by the reaction NH_4Br (solid) = NH_3 + HBr between 330 and 350°. *Ans.* About 26,000 cal. Calculate the total

ormula weights per liter at 350°, when the pressure is 237 mm. of mercury. *Ans.* 0.0048.

16. Hydrogen may be prepared by passing steam over hot iron and reezing out the remaining water. Assuming the reaction to be $Fe + H_2O = FeO + H_2$ at 1100° calculate the number of mols of steam required o make a mol of hydrogen. The dissociation constants are $K_{FeO} = 2.5 \times 0^{-13}$ and $K_{H_2O} = 3.5 \times 10^{-13}$ at 1100°.

17. What will be the composition of the gas phase in the previous problem f 2 mols of steam are heated with excess iron? How many mols of FeO ill be formed?

18. (*a*) Write the reaction which occurs when an excess of Ag_2CrO_4 is reated at 25° with 0.2 normal NaCl, and find the ratio $(CrO_4^=)/(Cl^-)$ in the olution at equilibrium. The solubility product for Ag_2CrO_4 is 10^{-10} and hat for AgCl is 1.2×10^{-10}. (*b*) By reference to this ratio discuss the ccuracy of the end point in the Volhard titration for chloride in the presence f K_2CrO_4 indicator. (The end point is taken when Ag_2CrO_4 begins to recipitate.)

19. The solubility of benzoic acid in water at 25° is 0.026 formal. Calcuate its solubility in 0.1 formal sodium acetate. $K_a = 1.8 \times 10^{-5}$ for acetic cid and 6.0×10^{-5} for benzoic acid.

20. The equilibrium constant of the reaction CuCl (solid) + Cl^- = $CuCl_2^-$ is 0.066 at 25° and 0.314 at 75°. Calculate the heat of solution of CuCl in dilute HCl. *Ans.* 6440 cal. absorbed per mol of CuCl.

21. Experiments on the solubility of zinc carbonate in water containing arbon dioxide in excess gave the following results at 25°, in mols per liter f solution:

Total CO_2	Total Zinc
0.1839	0.00211
0.4538	0.00291
0.7678	0.00343

a) Calculate the equilibrium constant of the reaction $ZnCO_3$ (solid) + $H_2CO_3 = Zn(HCO_3)_2$ at 25°. (*b*) The ionization constants of carbonic cid at 25° are $K_1 = 3.5 \times 10^{-7}$, $K_2 = 5.4 \times 10^{-11}$. Calculate the solubily product of zinc carbonate and the molal solubility of it in water on the ssumption of no hydrolysis. (*c*) Calculate the solubility of zinc carboate (*i.e.*, total zinc) in 0.25 formal carbonic acid solution. (The cubic quation so obtained is best solved by estimating a value of S, substituting in the equilibrium expression, and by trial determining whether the value too high or too low, estimating a new value, and repeating until a value is ound which satisfies the equation.)

22. The solubility of silver acetate in water at 16° is 0.060 formal. Calulate its solubility in 0.10 formal silver nitrate solution.

23. The solubility of thallous chloride in water at 25° is 0.0161 formal. alculate its solubility in 0.025 normal solutions of HCl, KCl, and Tl_2SO_4 by eans of the solubility-product law, and compare these calculated solubilities ith the experimental ones given in Table 96.

24. Cuprous chloride is practically insoluble in water and the solubility of cuprous chloride in 0.63 normal HCl at 25° is 0.039, due to the reaction $CuCl$ (solid) $+ Cl^- = CuCl_2^-$. The heat absorbed by this reaction is 6440 cal. Calculate the solubility of CuCl in 0.33 normal HCl at 35°. The experimental value is 0.0279.

25. The dissociation pressure of Ag_2O has the following values:

P (atm.)	20.5	32.0	74.3	114.5
T (abs.)	575	598	647	676

Calculate the heat absorbed by the reaction $2Ag_2O = 4Ag + O_2$, assuming it does not change with temperature and assuming oxygen an ideal gas.

26. The cooling curves of Fig. 63 are for atomic per cent of metal A in a certain system. Construct the phase diagram for this system over the

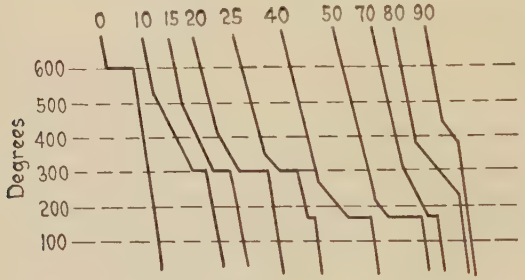


Fig. 63.

whole composition range, and letter each field to show what phases exist within it. Make reasonable estimates of quantities not given.

27. The cooling curves of Fig. 64 are for atomic per cent of metal A (m.p. = 425°) in B(m.p. = 750°). Construct the phase diagram for this

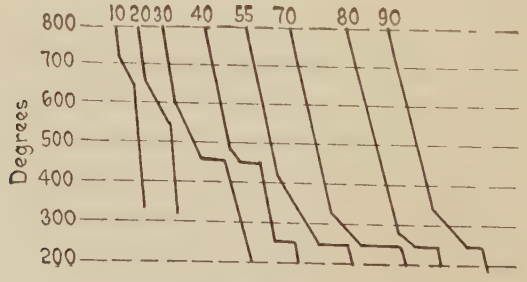


Fig. 64.

system over the whole composition range and letter each field to show what phases exist within it.

28. Draw a diagram showing quantitatively the change of volume with change of pressure for the compression of urethane at 60° described on page 305.

29. $CaCO_3$ dissolves in water containing CO_2 at 18° under pressure as follows:

Pressure CO_2 (atm.)	10	18	25	35
Per cent $CaCO_3$ by weight	0.256	0.307	0.342	0.380

Calculate the equilibrium constant $(Ca^{++})(HCO_3^-)^2/p_{CO_2} = K$ for 18° (HAEHNEL, *J. prakt. Chem.*, **107,** 165 (1924).)

30. Ammonium carbamate ($NH_4CO_2NH_2$) dissociates completely into NH_3 and CO_2 in the gaseous phase. The following data show the *total* pressure developed when it sublimes into excess NH_3 or CO_2 at various pressures.

Excess pressure		Total equilibrium pressure (in millimeters)
NH_3	CO_2	
0	0	88.5
13.3	....	88.1
26.9	....	89.4
....	20.4	90.2
....	35.2	97.4
....	91.7	137.3
....	167.5	202.4

Note that two-thirds of the increase over original pressure is due to NH_3 formed and calculate a set of values for dissociation constant. (BRIGGS and MIGRDICHIAN, *J. Phys. Chem.*, **28,** 1121 (1924).)

31. Picric acid ($C_6H_2(NO_2)_3OH$) distributes itself between water and benzol at 18° as follows:

C_W	0.0334	0.0199	0.0101	0.00327	0.00208
C_B'	0.1772	0.070	0.0199	0.00225	0.00093

What can be said of its molecular condition in the two solvents?

CHAPTER X

KINETICS OF REACTIONS

General Law.—The familiar reactions of inorganic chemistry proceed to completion almost instantly in many cases, but some of these reactions, and almost all of those of organic chemistry, require a measurable amount of time. When a one-way reaction is concerned, it approaches completion at a decreasing rate; when a reversible reaction is concerned, it approaches its equilibrium point at a decreasing rate. As a provisional statement of the law governing reaction rates, we may say that for a given temperature the rate at which a chemical reaction proceeds at any moment is proportional to the concentration of each of the reacting substances.

First-order Reactions.—To take as an example a reaction in which the concentration of only one substance is decreasing, sugar in dilute solution reacts with water to form glucose and fructose at a rate which is proportional to the sugar concentration. This rate is proportional to the water concentration as well, but the latter remains essentially unchanged throughout the reaction in a dilute solution. When half of the sugar originally present has been hydrolyzed, the rate of hydrolysis is half that of the reaction rate at the first instant when sugar was put into water. Such a rate may be expressed as mols per liter per minute. A reaction rate may also be defined as the rate at which the concentration of any reaction product is increasing. Let C denote the concentration of any product being formed in a reaction and let C_0 be the concentration of the reacting substance at the moment the reaction started. Then at any time, the concentration of reacting substance is the difference between that present at the start and that used in the reaction, or $(C_0 - C)$. In the reaction

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6,$$

the concentration of sugar when the elapsed time is 0 is C_0, that

after the time t is $(C_0 - C)$, and the concentration of glucose or fructose is C. The rate at which C is increasing is dC/dt, and this is the rate of the reaction. The expression for this rate is

$$\frac{dC}{dt} = k(C_0 - C). \tag{1}$$

This is also the expression for the velocity of any reaction in which only one reacting substance is changing its concentration. Its commonest application is when there is only one molecule of reacting substance involved in the chemical equation. If at some moment the concentrations of the reacting substance was 1 mol per liter, $(C_0 - C)$ would be 1 and the rate of the reaction would be equal to k. For this reason k is often called the specific reaction rate, or the rate at unit concentration. It will be sufficient for our purpose to consider it merely a proportionality constant.

Other reactions of the first order which have been studied carefully are the decomposition of nitrogen pentoxide[1] (N_2O_5) and of sulfuryl chloride[2] (SO_2Cl_2). Equation (1) above describes the rate of these reactions as a function of the concentration, since when measured values of time and concentration are substituted in the integral of this equation (the integration is explained below), a constant is obtained for k.

Order of a Reaction.—The *order* of a reaction is the number of molecules of reacting substance involved in the chemical equation which change their concentration during reaction. For example, the reaction of hydrogen iodide to form hydrogen and iodine is written

$$HI + HI = H_2 + I_2,$$

since two molecules of hydrogen iodide are required to form one molecule of hydrogen. This is a *second-order* reaction, and equation (1) above will not describe its velocity. In the sugar equation, two molecules are involved, but only one is changing its concentration. The order of a reaction ordinarily is the number of molecules of reacting substance appearing on the left-

[1] DANIELS and JOHNSTON, *J. Am. Chem. Soc.*, **42**, 53 (1921); HUNT and DANIELS, *J. Am. Chem. Soc.*, **47**, 1602 (1925).

[2] SMITH, *J. Am. Chem. Soc.*, **47**, 1862 (1925).

hand side of the chemical equation expressing the change taking place.

Catalyzers.—Substances which accelerate a reaction without appearing in the equation for it and without being changed by the reaction are called catalyzers. Acids increase the velocity of sugar hydrolysis but are not changed in concentration by the reaction; so, to a smaller extent, do bases. Fine platinum powder (platinum black) accelerates many gaseous reactions, but remains unchanged by them; yeasts and enzymes increase the velocity of fermentation and of digestive processes by catalysis. Often the manner of this aid in reaction is completely unknown; in a few cases it has been shown that the catalyzer reacts with some of the reacting substances, forming an intermediate product, which then reacts with the remaining substances to regenerate the catalyzer and complete the reaction. In other cases the mere presence of a catalyzer accelerates a reaction when no intermediate product can be discovered. It is likely that solid catalyzers adsorb gaseous or dissolved reacting substances on their surfaces in a higher concentration than exists in the bulk of reacting mixture, and discharge the products into the reaction space, but this explanation is doubtless incomplete for many reactions. Usually the accelerating effect is proportional to the surface of catalyzer exposed to a reacting mixture. This may be illustrated by the effect of adding cobalt peroxide to a solution of sodium hypochlorite,[1] which is catalytically decomposed by it. The reaction conforms to the first-order equation (2) given below, and the change in reaction constant K is proportional to the quantity of catalyzer, as shown in Table 102.

TABLE 102.—CATALYZER SURFACE AND REACTION CONSTANT

Amount of catalyzer	K	Ratio, $\times 10^{-3}$
2.5	0.00895	3.58
5.0	0.0176	3.52
7.5	0.0261	3.48
10.0	0.0348	3.48
12.5	0.0440	3.52
15.0	0.0523	3.49

[1] HOWELL, *Proc. Roy. Soc. London*, (*A*)**104,** 134 (1923)

Sugar Hydrolysis.—The hydrolysis of sugar at any temperature is accelerated by the presence of acids (hydrogen ions), and the extent of this increased velocity is proportional to the hydrogen ion concentration. Thus for this reaction we may write

$$\frac{dC}{dt} = k(\mathrm{H^+})(C_0 - C), \qquad (1a)$$

where k is the reaction constant or proportionality constant. $(\mathrm{H^+})$, the hydrogen ion concentration, is also a constant for any given experiment, since the catalyzer concentration is unchanged, and we may write these two constants as one single constant K,

$$\frac{dC}{dt} = K(C_0 - C),$$

which is the first-order equation; but we must remember that K is now dependent upon the hydrogen ion concentration, and that in applying the equation to experimental data, agreement between calculation and experiment is not to be expected if the acid concentration is not the same throughout a series of experiments. Separating the variables and integrating between the limits $t = 0$ and any time t, the corresponding limits for the concentration of any reaction product being 0 and C, we have

$$\frac{dC}{(C_0 - C)} = \frac{-d(C_0 - C)}{(C_0 - C)} = Kdt,$$

$$ln\frac{C_0}{(C_0 - C)} = Kt \text{ or } 2.303 \log\frac{C_0}{(C_0 - C)} = Kt. \qquad (1b)$$

The integral just given was obtained by integrating between the limits $t = 0$, when $C = 0$, and the concentration C at the time t. If it is desired to calculate the concentration at one time from that at another, this equation may be integrated between t_1 and t_2, for which the equation is as follows:

$$2.303 \log\frac{C_0 - C_1}{C_0 - C_2} = K(t_2 - t_1),$$

where C_1 and C_2 correspond to the concentration of any reaction product at t_1 and t_2, respectively.

It is often convenient to express the extent of a reaction at a given time as the fraction of reacting substance decomposed, x. Since in the equation one molecule of sugar forms one of glucose, C mols of sugar have been decomposed when C mols of glucose have formed, and the fraction of the sugar which has reacted is,

therefore, $C/C_0 = x$. Upon dividing both numerator and denominator of the fraction in equation (1*b*) by C_0 we obtain

$$2.303 \log \frac{1}{1 - x} = Kt. \qquad (2)$$

This equation will be useful in calculating reaction constants from experimental data.

The velocity of sugar hydrolysis is generally followed by observing the change in optical rotatory power of the solution. For when a beam of plane-polarized light is passed through a sugar solution, its plane of vibration is rotated toward the right through an angle proportional to the concentration of sugar in solution; polarized light is rotated in the opposite direction by the products of sugar hydrolysis. As the sugar concentration decreases, and that of the reaction products increases, the plane of rotation is changed, and the fraction of sugar decomposed is readily calculated for any time, since it is the quotient of the change in rotation up to that time divided by the total change in rotation when the reaction is completed, Let α_0 and α_f represent the initial rotation and final rotation, respectively, and let α_t represent the rotation at any time t. Then x, the fraction of sugar decomposed at t, is $\frac{\alpha_0 - \alpha_t}{\alpha_0 - \alpha_f}$. Substituting this value of x in equation (2), and combining the catalyzer concentration with the factor 2.3 (logarithmic conversion factor) in the constant of reaction, leads to the following expression for the reaction constant in terms of observed rotations:

$$K' = \frac{1}{t} \log_{10} \frac{\alpha_0 - \alpha_f}{\alpha_t - \alpha_f}.$$

Table 103 shows the results of experiments at 30° on sugar solutions in which the catalyzer is 2.50 molal formic acid. It will be observed that the values of K' are constant, and independent of the sugar concentration or the extent to which the reaction has progressed.

Another reaction of the first order is the conversion of hydroxyvaleric acid into valerolactone in the presence of an acid catalyzer,[1] the reaction being followed by titrating samples removed at intervals. As the reaction proceeds, hydroxyvaleric acid disappears and the titration of a sample of definite volume requires

[1] Taylor and Close, *J. Am. Chem. Soc.*, **39**, 422 (1917).

TABLE 103.—SUGAR HYDROLYSIS AT 30° IN 2.5 MOLAL FORMIC ACID[1]

Initial sugar concentration 0.44 molal			Initial sugar concentration 0.167		
Elapsed time (hours)	Rotation of plane of light	$K' = \frac{1}{t}\log\frac{\alpha_0 - \alpha_f}{\alpha_t - \alpha_f}$	Elapsed time (hours)	Rotation of plane of light	$K' = \frac{1}{t}\log\frac{\alpha_0 - \alpha_f}{\alpha_t - \alpha_f}$
0	(57.90)	.....	0	(22.10)	
2	53.15	0.0146	2	20.30	0.0146
4	48.50	0.0149	5	17.85	0.0145
6	44.40	0.0147	10	14.15	0.0148
8	40.50	0.0147	15	11.10	0.0147
11	35.20	0.0146	20	8.65	0.0145
15	28.90	0.0146	26	6.00	0.0146
21	20.70	0.0146	30	4.50	0.0147
27	13.50	0.0149	39	1.90	0.0146
35	6.75	0.0148	45	0.35	0.0149
40	3.40	0.0147	59	−1.80	0.0146
46	− 0.40	0.0149	73	−3.20	0.0148
52	− 2.95	0.0148	94	−4.30	0.0147
66	− 7.45	0.0146	133	−5.10	0.0147
85	−11.25	0.0146	Complete	−5.50	
112	−13.80	0.0147			
Complete	−15.45				

less and less standard alkali. Complete reaction corresponds to titrating the catalyzer only; hence the fraction of hydroxyvaleric acid decomposed at a time t is obtained by subtracting the volume of alkali used at that time from the volume employed in the initial titration, and dividing this difference by the difference between the first titration and that corresponding to complete reaction. The alkali concentration need not be known. Two series of experiments are shown in Table 104.

Here, as in other cases where a catalyzer is employed, the reaction constant as calculated above includes the concentration of catalyzer in the reaction constant. These experiments were repeated under exactly similar conditions except that the hydrochloric acid concentration was varied, and it was found that the velocity constant is proportional to the acid concentration,

[1] ROSANOFF, CLARK and SIBLEY, *J. Am. Chem. Soc.*, **33**, 1911 (1911).

Table 104.—Conversion of Hydroxyvaleric Acid into Valerolactone by 0.025 Normal Hydrochloric Acid at 25°

Time, minutes	Titration, cubic centimeters	$10^4K'$	Time, minutes	Titration, cubic centimeters	$10^4K'$
0	19.04	.....	0	18.55	
48	17.60	17.2	46	17.11	17.1
76	16.90	17.0	125	15.18	17.1
124	15.80	17.2	174	14.22	17.2
204	14.41	17.3	221	13.49	17.2
238	13.94	17.3	262	12.97	17.1
289	13.37	17.15	307	12.45	17.2
Complete	10.71	.....	Complete	9.87	

with only a slight variation. The figures obtained are shown in Table 105.

Table 105.—Catalyzer Concentration and Velocity Constant

Concentration of catalyst	10^4K	Ratio
0.10*N*	67.7	677
0.05	34.3	686
0.025	17.14	686
0.010	6.83	683

At higher acid concentrations the proportionality is not so good, and the explanation is not definitely known. Some authorities assert that hydrogen ions act as the catalyst, and in some reactions a better ratio of reaction constant to catalyst concentration is obtained when the activity of hydrogen ion is employed. A separate catalytic effect due to the non-ionized acid molecules has been postulated to explain the data, and is doubtless responsible for some of the observed effects. A full explanation of catalysis is yet to be discovered.

Second-order Reactions.—A reaction of this type which has been carefully studied is that between an ester and sodium hydroxide[1] in dilute solution, for example,

$$NaOH + C_2H_5OCOCH_3 = NaOCOCH_3 + C_2H_5OH.$$

[1] Walker, *Proc. Roy. Soc. London*, (*A*)**78**, 157 (1906).

The rate of this reaction at a given temperature is proportional to the concentration of ester and to the concentration of alkali, that is,

$$\frac{dC}{dt} = kC_{\text{ester}}\, C_{\text{alkali}},$$

where C denotes the concentration of alcohol formed. If at the start the concentration of ester is C_e and that of sodium hydroxide is C_a, the rate may be expressed in terms of a single variable C by noting that at any moment the concentration of ester is $C_e - C$ and that of the alkali is $C_a - C$. The equation is then

$$\frac{dC}{dt} = k(C_e - C)(C_a - C) \tag{3}$$

and the integral of this equation between the time limits 0 and t is

$$\frac{2.303}{(C_e - C_a)} \log \frac{C_a\,(C_e - C)}{C_e\,(C_a - C)} = kt. \tag{4}$$

This equation was derived for the case in which the original concentrations of the reacting substances were not assumed to be equal, and it cannot be transformed in terms of the fraction decomposed. For an equal number of *mols* of each substance react, and this will not be the same *fraction* of the original quantity for each.

For the special case of a second-order reaction when the original concentrations are equal, the differential equation above becomes

$$\frac{dC}{dt} = k(C_0 - C)^2$$

and its integral is

$$\frac{C}{(C_0 - C)C_0} = kt. \tag{5}$$

Upon dividing both numerator and denominator of the fraction by C_0 and noting that C/C_0 is x, the fraction decomposed, we have

$$\frac{x}{1 - x} = kC_0t. \tag{6}$$

In treating any given set of experimental data the constants k and C_0 may be combined into a single constant K if desired. Data

illustrating this equation are shown in Table 106, corresponding to the reactions

$$CH_3COOCH_3 + NaOH = CH_3OH + NaCOOCH_3$$

and

$$C_2H_5COOCH_3 + NaOH = C_2H_5OH + NaCOOCH_3.$$

The esters and alcohols are not ionized and do not, therefore, conduct the electric current; measuring the conductance of the reaction mixture, therefore, shows the extent to which sodium hydroxide has been replaced by the poorer conductor, sodium acetate. If the reacting substances are present in equivalent quantity, complete reaction corresponds to complete replacement of hydroxyl ion (equivalent conductance at 25°, 192) by acetate ion (equivalent conductance 40.8); that is, a change from a conductance proportional to the limiting values for sodium and hydroxyl ions (50.9 + 192 = 242.9) to one proportional to the conductances of sodium and acetate ions (50.9 + 40.8 = 91.7), or a decrease of over 60 per cent. The fraction of sodium hydroxide changed to acetate at any moment is, therefore, $(L_0 - L_t)/(L_0 - L_f)$, where the symbols represent the initial, temporary, and final observed specific conductances. Using this method of measuring reaction velocities, the following data have been obtained for solutions which at the start were 0.01 formal in sodium hydroxide and 0.01 formal in ester.[1]

TABLE 106.—SAPONIFICATION OF ESTERS AT 25°

Ethyl acetate			Methyl acetate		
Time, minutes	Fraction saponified	$kC_0 = \frac{1}{t} \cdot \frac{x}{1-x}$	Time, minutes	Fraction saponified	$kC_0 = \frac{1}{t} \cdot \frac{x}{1-x}$
5	0.245	0.0649	3	0.260	0.117
7	0.313	0.0651	5	0.366	0.115
9	0.367	0.0645	7	0.450	0.117
15	0.496	0.0650	10	0.536	0.115
20	0.566	0.0652	15	0.637	0.117
25	0.615	0.0642	21	0.712	0.118
33	0.680	0.0644	25	0.746	0.118

[1] WALKER, *Proc. Roy. Soc. London*, (*A*) **78**, 157 (1906).

A reaction involving two molecules of the same substance would also be considered as a second-order reaction. For example, the velocity of the reaction

$$2H_2O_2 = 2H_2O + O_2$$

in quinoline solution conforms more closely to the second-order than to the first-order equation, as shown by the data in Table 107. Under K_1 the "constants" obtained by substituting in the first-order equation are given, and under K_2 those for second-order. The data are not very conclusive and the reaction should be given closer experimental study.

TABLE 107.—RATE OF DECOMPOSITION OF HYDROGEN PEROXIDE IN SOLUTION IN QUINOLINE[1]

(A small quantity of manganese acetate has been added to accelerate the reaction)

Time (minutes)	Cubic centimeters oxygen evolved	K_1	C_0K_2
4.9	11.8	0.0693	0.816
6.6	14.3	0.0649	0.806
9.2	18.0	0.0626	0.844
11.7	20.7	0.0598	0.863
18.9	25.7	0.0506	0.878
22.5	27.4	0.0487	0.882
27.3	29.5	0.0461	0.854
30.8	30.2	0.0431	0.914
32.1	31.2	0.0384	0.975
Complete decomposition	41.2		

A similar change in the "constant" for the bimolecular reaction by which nitrous oxide decomposes[2] has been observed. The reason for this drift is not known in either case.

If a reaction occurs in steps taking place at widely different speeds, the measured velocity will be that of the slowest step. For example, hydrogen peroxide is decomposed catalytically by iodides, and the velocity is proportional to the first power of the H_2O_2 concentration. It is proportional to the iodide concentra-

[1] WALTON and JONES, *J. Am. Chem. Soc.*, **38**, 1959 (1916).

[2] HINSHELWOOD, *Proc. Roy. Soc. London*, (*A*) **106**, 284 (1924).

tion as well, but this remains constant during a reaction. It has been suggested by Bredig and Walton[1] that the slow reaction is

$$H_2O_2 + I^- = H_2O + IO^-$$

and that this is followed by the practically instantaneous reaction

$$IO^- + H_2O_2 = H_2O + I^- + O_2$$

which regenerates the iodide ions. In Table 108 are given data[2] for the decomposition of H_2O_2 in the presence of 0.02 normal KI.

TABLE 108.—DECOMPOSITION OF HYDROGEN PEROXIDE

Time	Fraction decomposed	$K = \frac{1}{t} \log \frac{1}{1-x}$
5	0.130	0.0124
10	0.242	0.0122
15	0.339	0.0116
25	0.497	0.0119
35	0.620	0.0120
45	0.712	0.0120
55	0.782	0.0121
65	0.835	0.0120
75	0.885	0.0125

It will be seen that these data correspond with a first-order reaction. Since the concentration of iodide ion remains constant, its concentration has been included in the value of K.

Reactions of Higher Orders.—Let the general equation for a reaction of any order be

$$aA + bB + eE + \ldots = \ldots;$$

then the velocity expression for this reaction is

$$\frac{dC}{dt} = k(C_a - C)^a(C_b - C)^b(C_e - C)^e \ldots, \qquad (7)$$

where C is the concentration of the reaction product. No general integral for this equation can be given. For a third-order reaction where the starting concentrations are equal, the equation becomes

$$\frac{C_0^2 - (C_0 - C)^2}{C_0^2(C_0 - C)^2} = 2kt \qquad (8)$$

[1] *Z. physik. Chem.*, **47**, 185 (1904).

[2] HARNED, *J. Am. Chem. Soc.*, **40**, 1467 (1918).

or, in terms of the fraction of each substance used at any time, when all of the initial concentrations are equal,

$$\frac{x(2-x)}{(1-x)^2} = 2ktC_0^2 = Kt. \qquad (9)$$

The reaction between nitric oxide and oxygen,[1]

$$2NO + O_2 = 2NO_2,$$

is of the third order, since it involves two molecules of nitric oxide and one of oxygen. By treating an extended series of measurements according to equation (9) it was found that K, the reaction constant, is 36.3 at 0°, 25 at 25°, 17.6 at 50°, and 11.2 at 86°. The constants obtained at any one temperature were very concordant, showing that equation (9) represents the true law of reaction velocity, and that this reaction is one involving three molecules.

Mechanism of a Reaction.—When the equations given above are applied to chemical reactions, cases are encountered in which the "order" of a reaction is not that to be expected from its chemical equation. As there is ample confirmation of the truth of the equations, the reactions under consideration must take place in steps. Thus suppose a given reaction to be taking place in two steps, of which the first was measurably slow and the second was practically instantaneous; observations would show the velocity of the first step alone. The case of hydrogen peroxide in the presence of iodides has already been given. Another case in point is the reaction

$$2HgCl_2 + H_3PO_3 + H_2O = 2HgCl + H_3PO_4 + 2HCl$$

which appears to be of the third order, since the water concentration does not change. Experiments[2] show that this process takes place in two steps, of which the first is the time-reaction and the second is fast enough to remove the products of the first almost instantly. The first step is

$$HgCl_2 + H_3PO_3 = HgCl + HCl + H_2PO_3$$

which is followed by the very fast reaction

$$2H_2PO_3 + H_2O = H_3PO_3 + H_3PO_4.$$

[1] WOURTZEL, *Compt. rend.*, **170**, 229 (1920).
[2] LINHART, *Am. Chem. J.*, **55**, 354 (1913).

Such velocity experiments therefore throw light on the actual process by which a chemical reaction occurs, while the chemical equation shows only the final result of the process.

Reversible Reactions.—The equations given above apply equally well to reversible reactions. Thus the velocity of the reaction $N_2O_4 = NO_2 + NO_2$ is proportional to the concentration of nitrogen tetroxide,

$$\frac{dC}{dt} = \kappa_1(C_0 - C);$$

and the velocity of the reverse reaction, $NO_2 + NO_2 = N_2O_4$, is proportional to the square of the concentration of NO_2,

$$\frac{dC'}{dt} = k_2(C_0' - C')^2.$$

At equilibrium these velocities must be equal, since no change in the concentration of any molecular species is observed. Upon equating them, and writing for $(C_0 - C)$ its equal (N_2O_4), and for $(C_0' - C')$ its equal (NO_2), we have

$$\frac{dC}{dt} = \frac{dC'}{dt} \text{ or } k_1(N_2O_4) = k_2(NO_2)^2,$$

whence

$$\frac{(NO_2)^2}{(N_2O_4)} = \frac{k_1}{k_2} = K,$$

which is the mass-action expression corresponding to the chemical equation $N_2O_4 = 2NO_2$. This discussion should not be considered as a "derivation" of the law of mass action, but merely a demonstration that apparently stationary equilibrium is not incompatible with a finite velocity of reaction in each direction.

Suppose a general reversible reaction to be $a + b = c + d$, and consider that we start with a and b present at equal concentrations. Then the initial rate of this reaction is the rate at which the concentration of c or d is increasing. As soon as any c and d have been formed, the reverse reaction by which they reform a and b can commence. As the concentrations of c and d are small at first, while those of a and b are comparatively much larger, the reaction proceeds rapidly toward the formation of more c and d. With increasing concentrations of these substances, the reverse rate increases, while with increasing concentrations of c and d the rate of their formation from a and b

decreases. After a time the reaction rates are equal, and equilibrium is reached. At equilibrium, each reaction is proceeding independently, but the concentrations are not changing, because the reaction rates are equal.

Effect of Temperature.—Nearly all chemical reactions proceed more rapidly at higher temperatures than at lower ones. The general effect consists in doubling the velocity of reaction for a rise in temperature of about 10°, though in some cases the speed is multiplied by 2.5 or even 3.5 for a rise of 10°. Many biological reactions have a maximum velocity at some characteristic temperature, but it is not certain that the decreased velocity at higher temperatures is a chemical effect. Excluding these from consideration, the rate of change of velocity is that stated above. An empirical equation expressing this change in the velocity constant for any particular reaction, due to van't Hoff, is

$$\frac{d \log k}{dT} = \frac{A}{T^2}.$$

The usefulness of this equation is much restricted, since the constant A must be determined from experiment for each reaction at two different temperatures. It is of service in interpolating for temperatures between those represented in a series of experiments, where the constant A may be evaluated from data at any two temperatures after the equation is integrated between limits. The method of integration is the same as that for the Clausius-Clapeyron equation on page 79 and the integrated form is

$$\log \frac{k_2}{k_1} = A\left(\frac{1}{T_1} - \frac{1}{T_2}\right).$$

To illustrate the use of this equation, refer to the reaction constants for nitric oxide oxidation (page 341); let 36.3 and 273° absolute correspond to k_1 and T_1, and 25 at 298° absolute, correspond to k_2 at T_2. Substitution into the above equation leads to $A = -1214$. By means of this value the reaction constant for 50° may be calculated from that at 25° to be 18.0; the measured value of the reaction constant at 50° is 17.6. However, this value of A is applicable only to the reaction in question, not at all to some other reaction over this temperature range.

Another test of this equation may be based on the monomolecular reaction[1] of which the result is

$$N_2O_5 = N_2O_4 + \tfrac{1}{2}O_2,$$

though it is probable that the reaction takes place in steps. However, the experimental data show conclusively that the reaction is a monomolecular one. In Table 109 are given the reaction constants at various temperatures, together with those calculated by van't Hoff's equation from the experimental value at 25°. The numerical value of A is 24,790 for this reaction.

TABLE 109.—CHANGE OF VELOCITY OF REACTION WITH TEMPERATURE

Temperature	10^3K	
	Observed	Calculated
0°	0.047	0.0444
25	2.03	
35	8.08	7.9
45	29.9	28.3
55	90.0	93.2
65	292.	286

Another expression for calculating the specific reaction constant at one temperature from that at some other temperature[1] may be written

$$\frac{k_1}{k_2} = \left(\frac{T_1}{T_2}\right)^m,$$

where T_1 and T_2 are the absolute temperatures corresponding to the reaction constants k_1 and k_2, and m is 28.5. This equation was found to express the change of velocity with temperature for a variety of reactions. The reaction rate at 10° is 2.78 times that at 0°; the rate at 20° is 7.46 times that at 0°; and the rate at 30° is 19.3 times that at 0°.

The temperature coefficient of reaction velocity is surprisingly large. An increase of 10° in the temperature of a gaseous mix-

[1] DANIELS and JOHNSTON, *J. Am. Chem. Soc.*, **43,** 53 (1921); see also HUNT and DANIELS, *J. Am. Chem. Soc.*, **47,** 1602 (1925).

[1] HARCOURT, *Phil. Trans. Roy. Soc. London*, **212,** 187 (1913).

ture under ordinary conditions produces an increase in the mean velocity of the molecules which is less than 3 per cent, but it increases the reaction velocity 150 per cent or more. In his original discussion of the temperature effect Arrhenius[1] assumed that only the "activated" molecules in a mixture actually react, and that the velocity of a reaction is strictly proportional to the number of such molecules. Lewis[2] defines an activated molecule as one possessing more than a definite minimum of energy, and gives a relation similar to the van't Hoff equation for change of chemical equilibrium with temperature,

$$\frac{d \ln k}{dT} = \frac{q}{RT^2},$$

where q is the heat of activation; that is, the energy absorbed in raising the active molecules to energy contents greater than the average corresponding to the temperature in question. Either molecular collisions or the absorption of radiant energy offer opportunity for "activation" of the molecules required to explain observed effects.[3]

Questions

1. A solution 0.167 molal in sugar and 2.5 molal in formic acid has at 30° a rotation of 22.10°. Owing to the presence of acid in the solution, inversion takes place at such a rate that the angle of rotation of polarized light is 11.10° after 15 hr. and 0.35 after 45 hr. (*a*) Calculate the angle of rotation corresponding to complete inversion of the sugar, using the value of K from Table 103. (*b*) Calculate the time necessary for half of the sugar to be inverted. (*c*) The solution was 2.50 formal in formic acid, whose ionization constant is 2.10×10^{-4}. Calculate the hydrogen ion concentration in this solution, and estimate the time required for inverting half of the sugar when the catalyzing acid is 0.10 formal hydrochloric acid.

2. In a solution containing 0.1 mol of ethyl acetate and 0.1 mol of sodium hydroxide per liter, 10 per cent of the ester is decomposed in 15 min. at

[1] *Z. physik. Chem.*, **4**, 226 (1889).

[2] *J. Am. Chem. Soc.*, **47**, 1508 (1925).

[3] Lewis points out that radiant energy of nearly constant frequency (monochromatic light) cannot account for the high rate of activation required by experimentally determined rates; energy of a range of frequencies is required. Tolman, (*J. Am. Chem. Soc.*, **47**, 1524 (1925)) concurs in this belief, but states that activation by collisions is improbable. For an excellent discussion of the theory which postulates activated molecules, reference should be made to Tolman's paper and to that of Lewis quoted above.

10° and 20 per cent at 25°. How much would be decomposed in 5 min. at 55°?

3. A solution of sugar in 0.002 normal hydrochloric acid has at 40° a rotation of 22.28°. In 90 min. this has decreased to 19.77°, in 150 min. to 18.27°, in 210 min. to 16.83°, and after the inversion was complete, to −5.37°. Calculate the reaction constant. Calculate the rotation of the solution when the reaction had proceeded 3 hr. How long would it take for the rotation to become 0°?

4. How long would it take to convert 40 per cent of hydroxyvaleric acid into valerolactone at 25° in the presence of 0.075 normal hydrochloric acid? See the text for data.

5. In a mixture containing 1 mol of hydrogen and 1 of chlorine at 25° and 1 atmosphere 15 per cent is converted to hydrogen chloride in 10 min. under the influence of light. What fraction will have reacted at the end of 40 min.?

6. A sugar solution has an initial rotation of 22.1°; after 20 min. its rotation is 8.65°, after 1 hr. −1.80°, and at complete hydrolysis −5.50°. (*a*) Calculate two values of the reaction velocity constant. (*b*) How long would be required to hydrolyze half of the sugar?

7. A liter of a solution of N_2O_5 in CCl_4 at 40° decomposes with the evolution of oxygen at the following rate:

T (min.)	20	40	60	80	100	Complete
Cubic centimeters O_2	11.4	19.9	23.9	27.2	29.5	34.75

Show whether the reaction is of the first or second order from a set of reaction constants.

8. Nitrogen pentoxide decomposes slowly at 20° according to the equation (1), $N_2O_5 = \frac{1}{2}\ O_2 + N_2O_4$ and the reaction (2) $N_2O_4 = 2NO_2$ reaches equilibrium instantly. The equilibrium constant, $K_p = 69$, for the second reaction is for pressures in millimeters. The first reaction is monomolecular and therefore the rate at which the pressure of N_2O_5 decreases is given by the equation $-d\ ln\ p/dt = K = 100 \times 10^{-5}$, when pressure is in millimeters and time in minutes. If the initial pressure is 100 mm. and the reaction is carried out at constant volume at 20°, calculate at the end of 350 min. the partial pressure of the gases N_2O_5, N_2O_4, and NO_2.

9. In a solution at 65° containing 22.9 grams of ammonium cyanate per liter, urea is formed as follows:

Time in minutes	0	20	50	65	150
Grams of urea formed	0	7	12.1	13.8	17.7

The equation for the reaction is $NH_4CNO = (NH_2)_2CO$. (*a*) Determine the order of the reaction by calculating a set of values of the specific reaction constant. (*b*) Estimate the time which would be required to transform half of the cyanate to urea at 65 and at 25°.

10. Acetochloranilide is converted into parachloracetanilide by 0.479 normal HCl at 25° as shown in the table. Calculate specific reaction

velocity constants for both the first and the second order and thus determine to which order this reaction belongs.

Time (minutes)	Cubic centimeter reagent to react with 10-c.c. sample
0	10.95
7.67	9.21
15.82	7.71
32.18	5.37

11. The velocity constant for the (first-order) decomposition of NaOCl changes with the temperature as follows:

t	25°	30°	35°	40°	45°	50°
k	0.0093	0.0144	0.0222	0 0342	0.0530	0.0806

Show that this change takes place in accordance with van't Hoff's equation (HOWELL, *Proc. Roy. Soc. London*, (*A*) **104,** 134 (1923).

CHAPTER XI

PHYSICAL PROPERTIES AND MOLECULAR STRUCTURE

Much careful work has been done in an effort to express the physical properties of substances (such as density or molal volume, optical properties, capillarity) in terms of figures representing the constituent atoms. Where these attempts have met with success, a value is assigned to each atom, and by adding together all of the values for each atom in the compound, each taken the number of times that it occurs in the formula for the substance, a measure of the desired property is obtained. It may be said at once that the fruitfulness of this type of work has scarcely justified the expenditure of time upon it, except in a very few cases. Thus the differences in several properties in passing from member to member of an homologous series are often quite constant, and useful relations among the members of a single group of elements such as the alkali metals or the halogens are known in a few cases. But nothing approaching a complete solution of the relation of physical properties to molecular constitution in general has yet been discovered. Some of these relations are mentioned briefly in this chapter.

Additive Properties.—Mass is an example of a strictly additive property; the molecular weight of a substance is exactly the sum of weights of the constituent atoms. Volume is sometimes roughly an additive property, though some astonishing exceptions are known; heat capacity is nearly additive in most cases. In general, an additive property is one which may be computed from the number of atoms of each kind and from a figure assigned to each atom which expresses its effect in all cases.

Constitutive Properties.—All properties which are not additive are said to be influenced by chemical constitution. A few properties, such as optical rotatory power, are the effect of constitution alone; and only these properties are properly considered under such a heading. Properties which are both addi-

tive and constitutive generally require further investigation. Outside the field of organic chemistry constitutive influences have scarcely been studied at all; within this field they are properly the concern of the organic chemist, and the student is referred to organic chemistry textbooks for a consideration of optical activity.

Molecular Volumes.—If no expansion or contraction took place during chemical combination, the molecular volume of any substance could be computed by adding together the atomic volumes of its elements, and a ready means of computing the density would be available, since density is molecular weight divided by molecular volume. But the problem is not so simple; molecular volumes are far from additive properties in many cases. Thus the volume of a formula weight of cesium chloride is about 30 c.c. smaller than the volume of the uncombined metal alone. But the difference between the molecular volume of a cesium salt and the corresponding rubidium salt is roughly constant, indicating that the effective atomic volume of cesium in its compounds is about the same for all compounds, even though it is not that of the uncombined element. The approximate constancy of this atomic volume for salts of the alkali metals is shown in the following table.

TABLE 110.—MOLAL VOLUMES OF SOLID HALIDES

	Cl	Dif.	Br	Dif.	I
Li	20.5	*4.6*	25.1	*7.9*	33.0
Dif.	*6.5*		*8.0*		*7.9*
Na	27.0	*6.1*	33.1	*7.8*	40.9
Dif.	*10.5*		*10.2*		*12.3*
K	37.5	*5.8*	43.3	*9.9*	53.2
Dif.	*5.7*		*6.1*		*6.6*
Rb	43.2	*6.2*	49.4	*10.4*	59.8
Dif.	*−0.8*		*−1.5*		*−2.2*
Cs	42.4	*5.5*	47.9	*9.7*	57.6

In the case of organic compounds, somewhat simpler volume relations are found, for the variations in chemical affinity, as measured by contraction during combination, are much smaller. Thus a beginning could be made by studying the difference in

molecular volumes of members of homologous series, to obtain an average effective molecular volume for the —CH_2— group; then the effect of hydrogen could be determined by reduction at a double bond, the difference between an atomic volume of hydrogen and one of combined chlorine could be measured by the increase of volume attending substitution, etc. From such a procedure it has been found that the effective atomic volume of a carbon atom is 14.8 c.c., hydrogen 3.7, sulfur 25.6 (22 in rings), nitrogen 15.6 (10.5 in primary amines, 12.0 in secondary amines), chlorine 24.6, bromine 27, iodine 37 c.c. per atomic weight.[1] By adding together these volumes, each taken the number of times the atom occurs in a compound, a fair measure of its molecular volume is obtained. Such a procedure is somewhat uncertain,[2] as may be seen from the figures given by another investigator. The molecular volume of an aliphatic compound at its boiling point is

$$V = 10.5\ N_C + 5.25\ N_H + 10.5\ N_O + 0.25\ (N_C + 2)^2.$$

As higher members of homologous series are considered, the molecular volume approaches as a limit that of $(CH_2)_n$. From the figures first quoted above, the volume of one CH_2 group is $14.8 + 7.4 = 22.2$, and the density should therefore approach $14/22.2 = 0.63$, but the limit actually approached is 0.86. We may calculate from the second set of figures the density of nonyl alcohol ($C_9H_{20}O$) as $144/220 = 0.65$, the experimental value being 0.84. Thus it is seen that no very satisfactory solution of this problem has been reached. Still another set of atomic volumes has been computed;[3] carbon 11; hydrogen 5.5; chlorine 22.8; carbonyl oxygen, 12.2; hydroxyl oxygen 7.8 c.c. per atomic weight. Densities calculated from molecular volumes based on these figures are, however, considerably in error. Thus acetone should have a molecular volume $33 + 33 + 12.2 = 78.2$, and a density of $58.1/78.2 = 0.74$; experiment gives 0.792. Chloroform should have a molecular volume according to these figures of $11 + 5.5 + 3 \times 22.8 = 84.9$ and a density of $119.4/84.9 =$

[1] Gervais Le Bas has studied the volume relations of organic compounds in detail. A large volume describes the results ("Monographs on Physical Chemistry"), of which the averages are here quoted.

[2] Kaufmann, *Z. Elektrochem.*, **25,** 343 (1919).

[3] Smiles, "Relation of Constitution to Physical Properties," p. 112.

1.40, while experiment gives 1.52. From these figures the density of $(CH_2)_n$ which high members of homologous series should approach is 14/22 = 0.635, which is greatly in error.

Molecular volumes are not generally additive. They appear to be approximately so in the case of organic compounds on account of the nearly constant attraction exerted. Thus the volume of an atomic weight of oxygen in an organic compound varies from 4.7 to 12.0 c.c., depending upon its linking. The atomic volume of magnesium is 14 c.c., the molecular volume of magnesium oxide is 12 c.c., leading to the absurd conclusion that oxygen has a negative molecular volume.[1]

Molal Solution Volumes.—The change in volume which occurs upon solution of a substance has been investigated by many workers. When a salt dissolves in water, it is freed from the forces which hold it together as a solid, it dissociates into ions (for which the change in volume is only slight), and it has an opportunity to combine with some of the solvent. In the following table, the decrease in volume attending the formation of a

TABLE 111.—VOLUME CONTRACTION ATTENDING THE FORMATION OF A SOLUTION FROM WATER AND THE CONSTITUENT ELEMENTS OF THE SALT[2]

	Cl	Dif.	Br	Dif.	I
Li	19.6	*6.2*	13.4	*11.0*	2.4
Dif.	*10.6*		*10.7*		*10.6*
Na	30.2	*6.1*	24.1	*11.1*	13.0
Dif.	*11.4*		*11.3*		*11.2*
K	41.6	*6.2*	35.4	*11.2*	24.2
Dif.	*5.2*		*5.3*		*5.4*
Rb	46.8	*6.1*	40.7	*11.2*	29.6
Dif.	*7.9*		*8.0*		*8.2*
Cs	54.7	*6.0*	48.7	*11.4*	37.3

salt from its elements plus that which occurs when it dissolves in water to form a normal solution at 25° is shown. This decrease in volume in a dilute solution is the volume change when the ions are formed from the elements; in a strong solution the

[1] For a full discussion of changing atomic volumes see Richards, *Proc. Am. Acad. Arts Sci.*, **37**, 1397 (1901); *J. Am. Chem. Soc.*, **36**, 2417 (1914).

[2] BAXTER and WALLACE, *J. Am. Chem. Soc.*, **38**, 98 (1916).

volume change upon union of the ions is included, but this is shown to be small from the fact that the effective solution volume is nearly independent of concentration up to five molal solutions for alkali halides.

It will be noted that the difference between the molal solution volumes of the different chlorides and bromides is about 6.1 c.c., regardless of the alkali element; and that the difference between the solution volumes of lithium salts and corresponding sodium salts is 10.6 c.c. regardless of the halide. This indicates that the effective solution volume is an additive one for the two constituent ions of a salt. This is found to be the case, and the contraction per formula weight when a normal solution is formed may be distributed among the separate ions as shown in Table 112. From these values, it is possible to compute the volume contraction when a solution is formed from the elements of the salt and the contained water, merely by adding together the effects for the separate ions which result. It should be made clear that these contractions are not those observed when the salt is dissolved; they are the sum of two effects of which solution is the second, and formation of the salt from its elements the first.

TABLE 112.—VOLUME CONTRACTION ATTENDING THE FORMATION OF A MOLAL SOLUTION; EFFECT OF THE SEPARATE IONS AT 25°

Ion formed	Contraction, cubic centimeters per atomic weight	Ion formed	Contraction, cubic centimeters per atomic weight
Li^+	11.4	Cl^-	19.1
Na^+	12.4	Br^-	12.7
K^+	24.0	I^-	1.4
Rb^+	29.1		
Cs^+	37.2		

Molecular Refraction.—This may be defined as the product of molecular weight and specific refraction, $M(n-1)/d$, where M is the molecular weight, n is the index of refraction, and d is the density of the liquid. For organic substances it has been found that this molecular refraction is approximately the sum of atomic refractions, *i.e.*, values assigned to each element such

hat the sum of the values (each atomic refraction being multiplied by the number of atoms of the element in the molecule under consideration) gives the molecular refraction. For example, let us calculate the atomic refractions for carbon, R_C, and hydrogen, R_H, from the measured molecular refractions of pentane (25.23) and hexane (29.84). If atomic refractions are additive, the molecular refraction for pentane, whose formula is C_5H_{12}, should be $5R_C + 12R_H = 25.23$; that of hexane should be $6R_C + 14R_H = 29.84$; both of these equations are satisfied if R_H is 1.06 and R_C is 2.49. From similar calculations upon a large number of compounds, the average values $R_C = 2.490$ and $R_H = 1.066$ have been obtained;[1] the increment for each CH_2 group on ascending an homologous series is $R_{CH_2} = 4.622$. What value to assign to oxygen depends upon its linking in a compound; 2.137 for a ketone oxygen, 1.494 for hydroxyl oxygen (alcohols), 1.663 for ethereal oxygen. Some illustrations of the exactness of this law of additive refractions are given in Table 113, where the calculated molecular refractions are based on the

TABLE 113.—MOLECULAR REFRACTIONS OF ORGANIC COMPOUNDS

Substance	Formula	Molecular refraction		Difference, per cent
		Measured	Calculated	
n-Pentane	C_5H_{12}	25.23	25.24	0.04
n-Octane	C_8H_{18}	39.16	39.11	0.13
Cyclopentane	C_5H_{10}	23.12	23.11	0.04
Acetone	CH_3COCH_3	16.15	16.03	0.74
Methylethyl ketone	$CH_3COC_2H_5$	20.65	20.66	0.05
Diethyl ketone	$C_2H_5COC_2H_5$	25.18	25.29	0.44
n-Butyl aldehyde	C_4H_9COH	20.64	20.66	0.10
Methyl alcohol	CH_3OH	8.22	8.24	0.24
Ethyl alcohol	C_2H_5OH	12.74	12.87	1.02
n-Propyl alcohol	C_3H_7OH	17.52	17.49	0.17
iso-Amyl alcohol	$C_5H_{11}OH$	26.74	26.73	0.04
Methylal	$CH_3OCH_2OCH_3$	19.19	19.32	0.68
Ethylpropyl ether	$C_2H_5OC_3H_7$	26.95	26.90	0.18
Ethyl ether	$C_2H_5OC_2H_5$	22.43	22.28	0.67

[1] SWIETOSLAWSKI, *J. Am. Chem. Soc.*, **42**, 1945 (1920).

average atomic refractions just given. In unsaturated compounds an effect is assigned to the double bond which is treated as an atomic refraction and added to the other atomic refractions. This effect[1] is 1.73 for a double bond and 2.40 for a triple bond.

Molecular refractions of dissolved salts are nearly additive at all concentrations,[2] if it is assumed that no change in the refraction of water results when a salt is dissolved in it. The increase in specific refraction due to added salt, multiplied by the molecular weight of the salt, has a value which may be divided among the separate ions in the way shown in Table 114.

TABLE 114.—MOLECULAR REFRACTIONS OF DISSOLVED SALTS AT 25°, SHOWN AS AN EFFECT FOR THE SEPARATE IONS

Ion	H	Cl	Br	I	Li	Na	K
Atomic refraction.....	1.03	7.50	11.05	17.68	1.27	1.75	3.84

Boiling Points.—These generally increase from member to member of homologous series as shown in Fig. 65. It will be seen that the increase for a $—CH_2—$ group becomes smaller for higher members of the series. This is expressed by Young's equation, from which the boiling point of a member of an homologous series may be calculated from that of the next member of the series below it. Let T be the boiling point of a compound, and T' that of the next higher member. Then

$$T' = T + \frac{144.86}{T^{0.0148T}}.$$

This expression applies not only to hydrocarbons of the straight-chain type, but to their derivatives as well.

A given fractional change in pressure usually produces the same *fractional* change in the absolute boiling points of different substances, provided the change in pressure is not too large. Thus a decrease of 5 per cent in total pressure lowers the boiling point of

[1] EISENLOHR, *Z. physik. Chem.*, **75**, 605 (1911). His values for the other atomic refractions quoted above are R_C 2.418, R_H 1.100, R_{CH_2} 4.618, 2.211 for carbonyl oxygen, 1.643 for ethereal oxygen, 1.525 for hydroxyl oxygen, R_{Cl} 5.967, R_{Br} 8.865, R_I 13.90.

[2] BAXTER, *J. Am. Chem. Soc.*, **33**, 901 (1911).

water 1.4°, which is 0.37 per cent of its absolute boiling temperature, 373. This same decrease of pressure should lower the absolute boiling point of alcohol 0.37 per cent; the calculated lowering is 1.3°, that experimentally measured is 1.2°. In many cases the agreement is much better than this, but this fairly represents the average case. Some further illustrations are given on page 81.

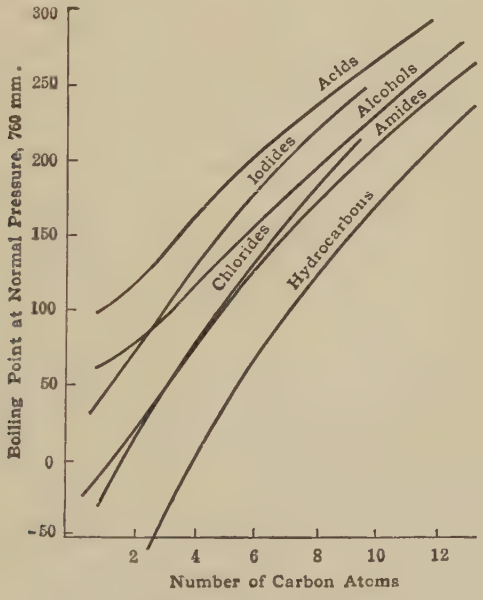


FIG. 65.—Boiling points in homologous series.

An elevation of boiling point usually results upon substitution of a higher boiling element in organic compounds; methyl chloride boils higher than methane, methyl iodide boils at a still higher temperature, and the same general effect is observed throughout a series.

Heats of Combustion.—Each higher member of an homologous series is formed from the one below it by adding a —CH_2— group; if the heat of combustion is an additive property, the difference for adjacent members in a series should be a constant, equal to the heat of combustion of one —CH_2— group. This heat of combustion has been estimated[1] at −153,500 cal.

[1] RICHARDS and DAVIS, *J. Am. Chem. Soc.*, **42**, 1616 (1920).

absorbed for each such group. The extent of variation to be expected is illustrated by the data for a series of alcohols.

The effect of constitution is clearly shown by the difference between the quantities of heat absorbed by a mol of butyl alcohol and a mol of its isomer. Other additive relations are considered briefly in connection with the bonds severed during combustion, for which see page 230.

TABLE 115.—HEAT ABSORBED BY COMBUSTION OF ALCOHOLS

Substance	Molal heat of combustion	Difference for CH_2
Methyl alcohol	−170,610	
Ethyl alcohol	−327,040	−156,430
Propyl alcohol	−485,800	−158,760
Butyl alcohol	−638,330	−152,530
iso-Butyl alcohol	−637,140	−151,340

Specific Heats.—The molecular heat capacity of a solid compound is approximately the sum of the atomic heat capacities of its elements. But as some elements which exist in solid compounds are not solids at room temperature, their atomic heat capacities in solids must be determined by experiment. Thus the difference between the atomic heat capacity of zinc and the molecular heat capacity of zinc oxide is 4 cal., and this is the effective atomic heat capacity of oxygen in solid oxides. Similar figures have been obtained for chlorine, sulfur, hydrogen, and other elements in an analogous way. It should be noted that solids of low atomic heat capacity (boron, sulfur, carbon) in the uncombined state retain these lower values in compounds. The average effective atomic heats are given on page 101, together with data illustrating the additive heat capacities.

CHAPTER XII

PERIODIC LAW OF THE ELEMENTS

Mendelejeff's periodic law states that when the elements are arranged in order of increasing atomic weight there is recurrence of chemical properties every eighth element. In some cases a recurrence of properties came in the seventh element, from which Mendelejeff rightly concluded that in this "period" there was a missing element yet to be discovered. By writing the elements in eight columns and leaving blank spaces where they seemed to be required in order to bear out the periodic law, he obtained the familiar periodic table. Of course, if an element should be discovered for which there was no blank place, an alteration in the periodic table would be made necessary. Just this thing happened in the discovery of argon, an element which did not resemble any known element; further researches brought to light a whole family of these elements, and another column was therefore made necessary in the table. The arrangement at present accepted is shown in Table 116. It contains three elements, gallium, scandium, and germanium, which were unknown to the discoverer of the periodic law; but he predicted the properties which these elements should have when discovered, and his predictions were confirmed by experiment after these elements were found.

The so-called rare earths disturb the periodic table unless several of them are assigned to a single place in the table; all of them have properties corresponding to this place and it seems proper that all of them should go in the one position. Eleven elements therefore occupy the place of lanthanum. Further study is needed to reveal the reason for this crowding of a single place; but the best that can be done at present is to leave all of them in this place. Indeed, if a similarity of properties is the basis of grouping elements in the periodic system, this similarity exists in the case of the rare earths to an extent

which makes their separation exceedingly tedious and difficult. Similar cases exist among the radioactive elements, where several elements occupy a single position in the periodic table; and the properties of elements in any one position are practically identical, so that effective separation has yet to be accomplished by any means. These elements have different atomic weights, but appear to be identical otherwise, while compounds of the rare-earth elements have properties (such as solubility) which differ very slightly from element to element.

There are other irregularities in the periodic arrangement of elements according to atomic weight which are difficult to understand, and for which there are no explanations at present. Iodine has a smaller atomic weight than tellurium and should therefore come in the column with sulfur, while tellurium then falls in the halogen column. It was at first thought that this indicated an error in the atomic weight determinations, but a large number of very careful experiments have shown that this is not the case. We therefore disregard the order based on atomic weight in making up the halogen column, and put iodine out of order so far as its atomic *weight* is concerned. It will be shown later that there is another property more fundamental than the weight of atoms, and that when the elements are arranged according to this property there is no such discrepancy; iodine falls in its proper place. Another pair of elements in the table is also out of order if the weight order is followed; argon should fall in the alkali metal column and potassium in the inert gas column. Here again the elements are placed in the column required by their chemical properties and the weight order is disregarded.

Leaving out of consideration the exceptions to this periodic law, the elements may be arranged in the way shown in Table 116. Under each element in this table is a number which is its order number in the periodic arrangement. Only the elements numbered 62, 85 and 87 have not yet been discovered, but the grouping which corresponds to the physical and chemical properties of the elements is disturbed unless blanks are left in the table for these elements. Thus, if radium emanation is element 85 and no blank is left, this member of the rare gas group is shown as a homologue of manganese, but it resembles manganese in none of its properties. These numbers are now quite gener-

ally called the atomic numbers of the elements. The exceptions to Mendelejeff's periodic law disappear when it is stated in the form: The chemical and physical properties of the elements are periodic functions of their atomic numbers. Atomic numbers are therefore of importance in the study of atomic structure.

Recently, quite definite proof that the atomic numbers are a fundamental property of the elements has been obtained from

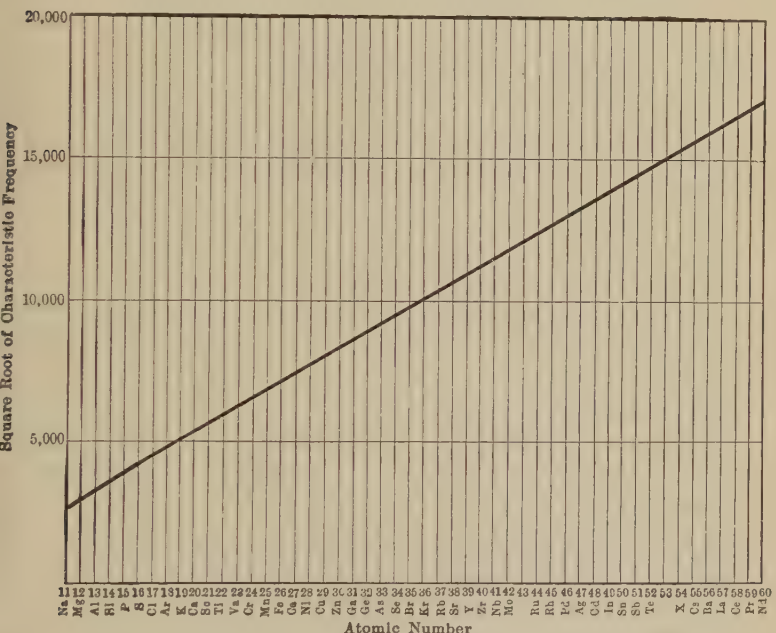

20,000
15,000
10,000
5,000
Square Root of Characteristic Frequency
11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60
Na Mg Al Si P S Cl Ar K Ca Sc Ti Va Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr Rb Sr Y Zr Nb Mo Ru Rh Pd Ag Cd In Sn Sb Te X Cs Ba La Ce Pr Nd
Atomic Number

FIG. 66.—Relation of atomic number to vibration frequency.

X-ray bombardment.[1] When the elements are used as targets for a stream of cathode rays of sufficient velocity, each element emits a series of monochromatic short-wave X-radiations of characteristic frequency. These radiations come from the very nucleus of the atom, on account of the violent bombardment. When the square root of the characteristic frequency for the various elementary substances is plotted against the atomic number, a straight line is obtained, as shown in Fig. 66; but this

[1] MOSELEY, *Phil. Mag.*, **26,** 1024 (1913); **27,** 703 (1914).

relation is disturbed if the order of the elements is that of atomic weights, just as flaws appear in the periodic table if the arrangement is that of atomic weights. Other evidence justifying the arrangement which best illustrates the periodicity and which ignores some weight factors will be given later; though it may be said here that the atomic numbers depend upon the fundamental structure of the nucleus of the atom.

Moseley's experiments also afford an indication of the number of elements yet to be discovered, since the straight line showing the relation between the square root of the vibration frequency and the atomic number would exhibit displaced sections if missing elements existed, and these displacements could be eliminated by leaving a blank space for the new elements. In this way it was found that from aluminum to gold there are only three elements missing, of atomic number 43, 61, and 75, corresponding to two homologues of manganese and one rare earth.

Many arrangements of the elements in plane diagrams, on spirals, and as space diagrams have been proposed from time to time since the first periodic law was announced. Each of these arrangements brings out some particular points better than a simple arrangement in columns, but does not contribute greatly to the subject as a whole. A recent representation of the arrangement on a helix in which the atomic weight is plotted vertically[1] brings out some additional points, and is shown in Fig. 67. In it the first two "short periods," consisting of the elements helium to fluorine and neon to chlorine, form a single loop each. Following this, the longer "periods" of 18 elements each (argon to bromine and krypton to iodine) are represented by two turns each on the helix. And to allow for the rare earths, the helix makes a short special loop back from cerium (element 58) to præseodymium (element 59) which is under lanthanum (element 57); following which all of the rare earths come under this point in a vertical line, corresponding to a change of atomic weight (and increase in atomic number) with only a very slight change in chemical properties. The several elements of radioactive origin corresponding to a single position in this table also appear in vertical groups; they are connected with brackets in the simple arrangement of Table 116.

[1] HARKINS, *J. Am. Chem. Soc.*, **38**, 169 (1916).

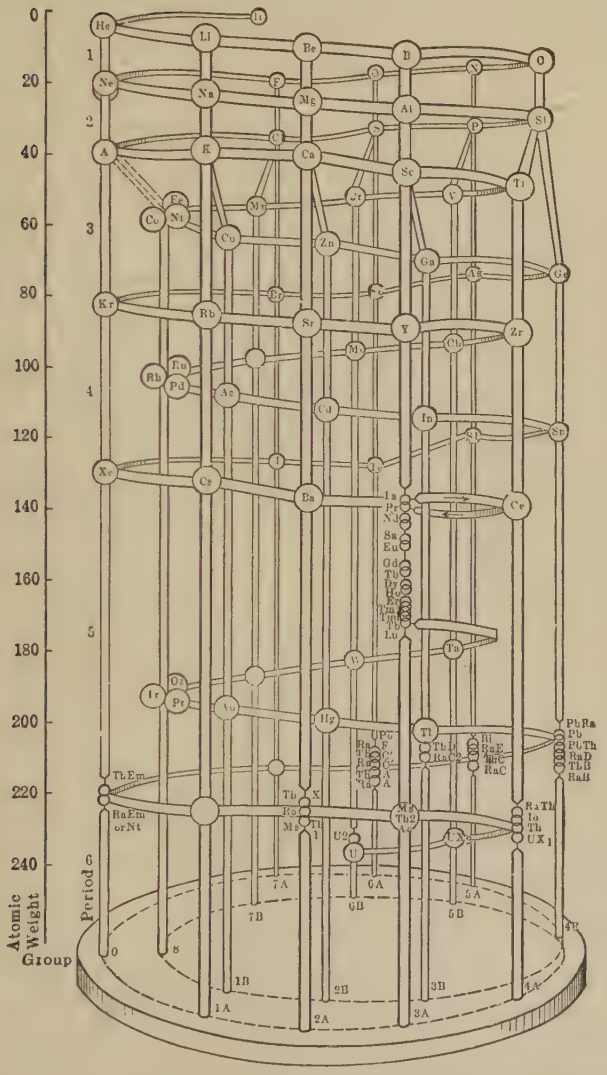


FIG. 67.—Harkins' model of the periodic arrangement of elements.

Periodic Properties of the Elements.—When the atomic volume, density, coefficient of expansion, latent heat, electrical conductivity, compressibility, melting point, boiling point, or

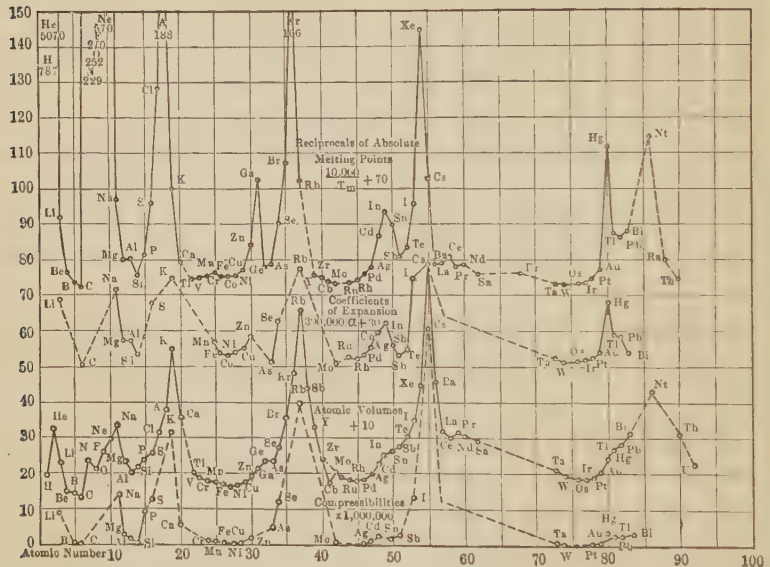


FIG. 68.—Periodic properties of the elements.

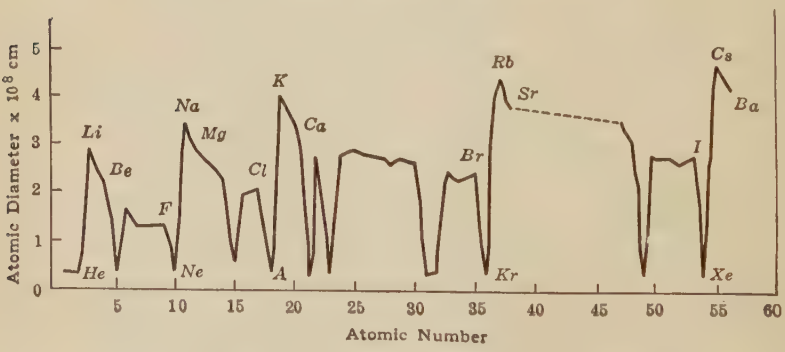


FIG. 69.—Relation of atomic number to atomic diameter.

any other physical property of the elements is plotted against the atomic number as abscissæ, a curve showing peaks and troughs periodically is obtained. Such a curve is shown for some properties in Fig. 68. If sodium occurs on a high peak, as in the

TABLE 116.—PERIODIC SYSTEM OF THE ELEMENTS[1]

Group 0 - - - -	Group 1 E_2O - -	Group 2 EO - -	Group 3 E_2O_3 - -	Group 4 EO_2 EH_4	Group 5 E_2O_5 EH_3	Grou EO EH
	H *1*					
He *2*	Li *3*	Be *4*	B *5*	C *6*	N *7*	O *8*
Ne *10*	Na *11*	Mg *12*	Al *13*	Si *14*	P *15*	
A *18*	K *19*	Ca *20*	Sc *21*	Ti *22*	V *23*	Cr *24*
	Cu *29*	Zn *30*	Ga *31*	Ge *32*	As *33*	
Kr *36*	Rb *37*	Sr *38*	Yt *39*	Zr *40*	Cb *41*	Mo *42*
	Ag *47*	Cd *48*	In *49*	Sn *50*	Sb *51*	
Xe *54*	Cs *55*	Ba *56*	La *57*	Ce *58*		
		Pr *59* Gd *64* Tm_I *69*	Nd *60* Tb *65* Tm_{II} *70*	- - *61* Ho *66* Yb *71*	Sa *62* Ds *67* Lu *72*	Eu *63* Er *68*
					Ta *73*	*74*
	Au *79*	Hg *80*	Tl *81* Ac D Th D Ra C_2	Pb Ra D *82* Ac B Th B Th D_2 Ra B Ra D_2	Bi Ra E *83* Ac C Th C_1 Ra C	Ra Ac *84* Ac Th Th Ra Ra
Ac Em Th Em Ra Em *86*	- *87*	Ac X Th X Ra Mes Th_1 *88*	Ac Mes Th_2 *89*	Rd Ac Rd Th Io Th Ux_1 *90*	Ux_2 *91*	U_{II} U_I

[1] Arranged according to DUSHMAN, *Gen. Elec. Rev.*, **18**, 614 (1915).

atomic volume curve, potassium, cesium, and the other elements of this group also occur on peaks; these alkali elements also occur on peaks of the compressibility curve, etc. While only a few physical properties are shown in the plot, a similar curve is obtained whatever property is studied. Thus it appears that whatever internal structure of atoms is responsible for their properties, this arrangement is reproduced to a large extent after the required number of additions to the atomic mass, though it does not follow that the increments of mass are responsible for the properties. This will be explained in a later chapter.

Recent work on the distance between atomic centers in crystals has led to values for the effective atomic diameters which, when plotted against the atomic number, give a curve showing the same periodicity as that of Fig. 68. This is shown in Fig. 69.

CHAPTER XIII

RADIOCHEMISTRY

The phenomena of radiochemistry differ in many ways from other types of chemical change, but they are real chemical changes which occur at a rate corresponding to the law for a monomolecular reaction. The changes are entirely irreversible, and their rates are quite beyond control by any known means; the energy effects accompanying them are far larger than those of ordinary chemical reactions, and there is a change in the *number of atoms involved* in such reactions. These reactions proceed at the same time as the ordinary chemical reactions of the substances, and are entirely independent of them. Thus as long as an atom of radium exists as such, it is capable of combining with halogens in the same way as barium does, or it will form an insoluble sulfate; but when it undergoes its radioactive change (atomic disintegration), it yields a charged helium atom and becomes an atom of inert gas belonging to the argon family. This is, therefore, an atomic transmutation of one element into two others.

Alpha Particles.—Whenever a radioactive change occurs, the atom emits a charged particle of some sort. An atom of helium bearing two units of positive electricity is called an alpha particle. More properly, the alpha particle is a helium atom which has lost two electrons, or unit negative charges. These particles are expelled from atoms with a velocity of about 10,000 miles per second, and when they are directed upon a screen of zinc sulfide, a luminescence is produced. Under the microscope this is seen to be composed of separate flashes, each due to the impact of a single alpha particle. By counting the flashes in a given area, and computing the total number of particles emitted upon the assumption that the emission was the same in all directions, it has been possible to determine the total number of particles emitted per second by a quantity of radium. Other experiments

have shown that these charged particles carry the same quantity of electricity as a positive bivalent ion in solution, that is, two units of positive electricity.

Beta Particles.—These are the other particles emitted during radioactive change; they consist of unit negative charges of electricity, and are not associated with matter of any kind. That is, they are "atoms" of negative electricity having no material substance, no mass. They are expelled with even greater velocity than the alpha articles; they approach but do not attain the velocity of light.[1]

Gamma Rays.—These also accompany radioactive changes, and they have been shown to be identical with X-rays; they are not particles, but short wave radiations like the rays produced in an ordinary X-ray tube. They result from the bombardment of the radioactive material by electrons which result from its decomposition, just as in an X-ray tube the rays result from bombardment of a target by a stream of electrons from a cathode.

Energy Effects of Radioactive Changes.—These are many times greater than those of ordinary chemical reactions. Rutherford has calculated that energy is emitted by an atomic weight of radium emanation at a rate equivalent to about 12,000 hp.,[2] and that the total energy evolved during its radioactive change

[1] The theory of relativity leads to an expression for the mass of a moving object as a function of its velocity v, its stationary mass m_0, and the velocity of light c. This expression is

$$m = \frac{m_0}{\sqrt{1 - (v^2/c^2)}}.$$

So long as the velocity is small compared to the velocity of light, m does not differ appreciably for m_0. But as v approaches c, the denominator becomes small and m approaches infinity. Thus it would require an infinite expenditure of energy to give a body of finite mass the velocity of light according to this equation. The greatest velocity imparted to a material object by any means within our control is about 2800 ft. per second, the muzzle velocity of a rifle bullet, which would correspond to an increase of about 10^{-12} in the mass of the projectile. The mass of an electron is about 0.0005 of that of a single hydrogen atom, but the kinetic energy of a particle of this size, so minute that 10^{27} of them weigh 1 gram, becomes considerable at high velocities. According to the equation above, it would require the expenditure of an infinite amount of energy to give a single electron the velocity of light.

[2] *Smithsonian Inst. Ann. Rept.*, **1915**, 167.

to the next element in the series is equivalent to the operation of a 60,000-hp. engine for one day. This is millions of times greater than the energy of the most violent chemical reaction involving the same weight of matter, about 220 grams, or less than half a pound; but it does not mean that one possessed of the required quantity of emanation could perform this quantity of work in a day by means of it, for the emanation decomposes at its own characteristic rate and cannot be made to undergo its change in a day. The emission of energy from atomic disruptions does not controvert the law of conservation of energy, for the energy is derived from the atom itself, where it exists in kinetic or potential form. Even if some means of reversing a radioactive change were known, the amount of energy required to effect atomic synthesis cannot be less than that evolved upon atomic disintegration.

Monomolecular Reactions.—Radioactive changes are true monomolecular reactions, the velocities of which are proportional to the quantity of substance present. Thus a given very small fraction of the radium atoms present (1 in about 100,000,000,000) break up with explosive violence each second, expelling a fragment of the atom (an alpha particle) with great speed. The residual atom is lighter than before, and has become the atom of an entirely new and different element, for radium is a solid metal similar to barium, and the new atom formed is a gas belonging to the rare gas family and incapable of *chemical* reaction.

This new substance, called radium emanation or radon, is capable of the same kind of a reaction as that which formed it; namely, an explosive disruption into another alpha particle or charged atom of helium, and a new residual substance called radium A. This latter element is very unstable, and breaks up at once, giving another alpha particle and forming a residual atom called radium B. Since in all three alpha particles of atomic weight 4 have been lost, there is a total decrease of 12 in the atomic weight from that of radium (226), and the atomic weight of radium B is, therefore, 214.

When radium B explodes, there is emitted an electron but no helium atom. This electron is a unit charge of negative electricity having no appreciable mass in the ordinary sense of the

term, and the atomic weight of the residual atom, radium C, is, therefore, the same as that of its parent element, 214.

For any one of these changes the rate is strictly proportional to the number of atoms present; or, in other words, a fixed fraction of the total number of atoms present at any moment decompose in a unit of time. This is expressed by the law of a first-order reaction (page 333),

$$ln \frac{1}{(1 - x)} = kt.$$

However, we have here a *monatomic* reaction, since only 1 atom is involved in producing both of the reaction products. From a table of specific reaction constants, k, for each reaction, it is possible to calculate the fraction decomposed in any interval of time. The common procedure is to compute and record the time required for half of the material to decompose, the so-called "period of half decay." Since the activity of a radium preparation (for example) depends upon the number of atoms decomposing each second, it is clear that in the half time for radium, its activity would drop to half of the original activity. When another period of this length had elapsed, the total activity is one-fourth of the original activity; one-eighth after the elapse of another such period, etc.

These changes differ from ordinary chemical reactions in that they are entirely uninfluenced by changes of temperature; a radium preparation decomposes at the same rate in liquid air as at a red heat, and regardless of the concentration or pressure. No method has yet been found of accelerating or retarding any radioactive change, that is, any atomic decomposition.

Counting Atoms.—It has already been shown (pages 64, 95, 115) that an atom is exceedingly small, and that it would be quite impossible to see a single atom or a particle containing a small number of atoms. There is, however, a means of observing the *effect* of a single charged helium atom or alpha particle, due to the great velocity (about 10,000 miles per second) with which it is discharged from radium in its decomposition. These particles are discharged in all directions, and produce a tiny flash of light when they impinge on a layer of zinc sulfide. Under a microscope it has been possible to observe the flash due to each

particle. This arrangement is called a spinthariscope. Knowing the size of the microscope field and its distance from the radium preparation, it is an easy matter to calculate the number of alpha particles shot out per second by the whole preparation, by means of the ratio of the area of the field to the whole spherical area which is bombarded at the same rate. The number of particles per second from a gram of radium is 1.36×10^{11}, as determined in this way.

Number of Atoms in a Gram-atomic Weight.—Since an alpha particle which has lost its charge is in no way different from a helium atom, it follows that radium produces helium at a definite rate. Experiments have shown that the helium so produced is 0.156 c.c. per year per gram of radium. Since we have counted the number of particles shot out per second and have measured the volume of gas, we have here a means of determining the number of atoms in a gram-atom of this monatomic gas. There are 3.15×10^7 sec. in a year; therefore, there are $1.36 \times 10^{11} \times 3.15 \times 10^7$, or 4.29×10^{18}, alpha particles expelled per gram of radium per year, and this is the number of molecules in 0.156 c.c., whence it follows that there are 2.75×10^{19} molecules per cubic centimeter, or 6.16×10^{23} per molecular volume.[1] There could hardly be a more convincing proof of the atomic structure of matter or of the number of atoms forming a given weight of helium, for the number of separate constituents has been counted and the volume has been measured. The value so obtained is in good agreement with other determinations of Avogadro's number, based upon quite different methods. It is remarkable that radioactivity measurements which have shown that the atoms of some elements are unstable should also furnish the most convincing proof of the atomic structure of matter and of the actual reality of atoms.

Radioactive Series.—It has been established after much careful work that the familiar activity of radium is but one step in a long series of atomic transformations, some of which occur with exceedingly great velocity, others of which occupy thousands of years. The atomic changes always consist in the expulsion from the atom of alpha particles (charged helium atoms) or beta particles (negative electrons), whether they are taking place

[1] RUTHERFORD, *Smithsonian Inst. Ann. Rept.*, **1915**, 181.

rapidly or slowly. In the following table, one such series is given in detail. Uranium, the first element in this long series of elements, changes so slowly that 5×10^9 years are required for half of it to decompose; the change consists in expelling an alpha particle, and the resultant atom is, therefore, lighter in atomic weight by four units. Reference to Table 118 shows that the new element, uranium X_1, is quite unstable, half of it decomposing in about 3 weeks. Since an atomic weight of uranium

TABLE 118.—RADIOACTIVE CHANGES IN THE URANIUM SERIES[1]

Element	Atomic weight	Chemical properties	Periodic group	Atomic number	Character of particle expelled	Half time value
Uranium 1.....	238	uranium	VI a	92	α	5×10^9 years
Uranium X_1 ...	(234)	as thorium	IV a	90	β	24.6 days
Uranium X_2 ...	(234)	(brevium)	V a	91	β	1.15 min.
Uranium 2.....	(234)	as uranium	VI a	92	α	10^6 years
Ionium.....	(230)	as thorium	IV a	90	α	10^5 years
Radium	226	like barium	II a	88	α	2,000 years
Emanation.....	222	none	0	86	α	2.85 days
Radium A	218	as polonium	VI b	84	α	3 min.
Radium B	(214)	as lead	IV b	82	β	26.7 min.
Radium C_1.....	(214)	as bismuth	V b	83	β	19.5 min.
Radium C'.....	(214)	as polonium	(VI b)	(84)	α	10^{-6} sec.?
Radium D.....	(210)	as lead	IV b	82	β	16 years
Radium E	(210)	as bismuth	V b	83	β	5 days
Radium F	(210)	polonium	VI b	84	α	136 days
Radium G	(206)	lead	IV b	82		

forms half an atomic weight of uranium X_1 in 5×10^9 years, and half of the amount present at any time decomposes in 3 weeks, it will be seen that uranium X_1 cannot be a familiar substance, and that its properties cannot be tested by ordinary chemical means, since only an exceedingly small quantity of it could be collected from any reasonable quantity of uranium.

The product of decomposition of uranium X_1 is uranium X_2, which is formed without loss of weight, since a beta particle is evolved; this element changes rapidly to uranium 2, a more stable element. At this point there is a branching in the chain of

[1] FAJANS, *Sci. Am. Supplement*, **81**, 83 (1916). Other writers give slightly different values for the period of average life. Compare SODDY'S textbook, or RUTHERFORD, *Smithsonian Inst. Rept.*, **1915**, 185; *Nat. Research Council Bull.* **10**, No. 51 (1925).

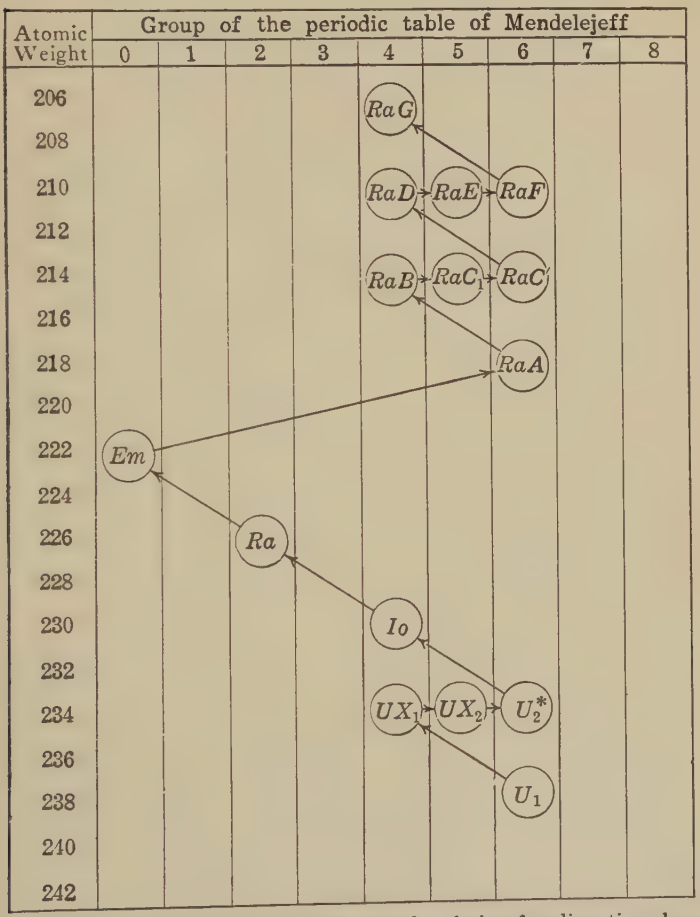
elements; only 92 per cent of uranium 2 follows the series as shown in the table. We have omitted consideration of the side series, which resembles the main one in general character, though it leads to the formation of different elements. It can be seen from study of Table 118 that the loss of an alpha particle always results in forming an atom lighter by four units than its parent, while the loss of a beta particle takes place without change in atomic mass. Those elements whose atomic weights are inferred from the character of radioactive change have been indicated in the table by enclosing the atomic weight in parentheses. Weights not in parentheses have been determined by the usual methods, as described in the first chapter of this book. The elements resulting from radioactive change have not, for the most part, been collected in sufficient quantities for direct chemical experiments; special methods of exceeding delicacy have been applied to determining their properties. Radium emanation has been obtained in small quantities sufficient to determine its density, and to prove that it is *chemically* inactive like the rare gases of the atmosphere. Some of the chemical properties of the other elements are inferred from their positions in the periodic table.

Radioactivity and the Periodic Table.—As may be seen from Table 119, the loss of an alpha particle shifts the position[1] of an element in the periodic table two places to the left, and the loss of a beta particle moves it one column to the right. Thus, the loss of one alpha particle and two beta particles brings an element into the column from which it started, but with a decrease of four units in atomic mass. It should, therefore, have properties similar to those of the parent element after such a change, and this is found to be the case. So far as their properties have been studied, there appears to be no *chemical* difference whatever between radium B, radium D, and radium G (supposed to be the stable element lead), though the atomic weights change by four units. Here we have definite proof that atomic mass is not the determining factor in chemical properties. In considering the periodic table in general, it was found necessary to follow the order of *atomic numbers* in arranging elements; the question arises, Will this settle the present difficulty? It will; but the settlement

[1] Soddy, *Nature*, **102**, 356 (1919).

s a little surprising, for these elements, radium B, radium D, and adium G, have the *same* atomic number, and therefore occupy

TABLE 119.—RADIOACTIVE CHANGES IN THE URANIUM SERIES, IN RELATION TO THE PERIODIC TABLE OF THE ELEMENTS



* At uranium 2 there is a branching in the chain of radioactive changes, and only 92 per cent of uranium 2 follows the changes here shown; the remainder undergoes a different set of decompositions of the same general character as those of the main series.

he *same* place in the periodic table. Since they behave chemically in exactly the same way, that is, as the same element, and

occupy the same place in the periodic table, why not call them all the same element? This might be done if the atomic weights were not different by four units. Can an atom yield an atom of helium upon disintegration, and then by the loss of two electric charges become again the same element? If its atomic weight is a fundamental property of an element, no; if chemical identity in every other way constitutes the governing factor, yes.

Isotopes.—Isotopic elements are identical in every way except atomic mass. That is, the elements radium B, radium D, and radium G are isotopes of lead; they have the same atomic number as lead, occupy the same place in the periodic table, are identical with it in chemical properties, are inseparable from it; but they are of different atomic mass. A specimen of "lead" in which some radioactive change is still going on would presumably contain some of radium D or radium B. As seen from Table 119, the atomic weight of radium G should be 206, since it is formed from radium (atomic weight 226) after the loss of five alpha particles, each of atomic weight four. The experimental value for the atomic weight of ordinary lead is 207.20, but as it is not in the least radioactive, it cannot be a mixture of these isotopes. The inactive end element of another disintegration series known as the thorium series is also an isotope of lead, with an atomic weight 208.1, and it might be possible that ordinary inactive lead is a mixture of these two inactive end products.

Several questions will occur at once. Can inactive lead ever be found with an atomic weight other than 207.2, due to mixture of inactive isotopes in different proportions? Can a substance chemically identical with lead, but of different atomic weight, be prepared from the lead of radioactive minerals? Can this radioactive lead be separated into two components, one of which is inactive lead of atomic weight 207.2? Can ordinary lead be separated into two components of atomic weight 206.0 and 208.1? The first and last of these questions may be considered together. Specimens of lead minerals from various parts of the world were collected,[1] and the lead in them was subjected to most careful purification by several different chemical processes. The atomic weights were found to be identical, and all of the specimens were found to be inactive lead. These results are shown

[1] BAXTER and GROVER, *J. Am. Chem. Soc.*, **37**, 1027 (1915).

n Table 120. If lead was separable into fractions of different tomic weights, this would have been brought out by the differnt methods of purification, some of which would eliminate one onstituent more completely than the others. If the two isoopes occur mixed in different proportions, this should be brought

TABLE 120.—ATOMIC WEIGHT OF INACTIVE LEAD FROM VARIOUS SOURCES

Source of lead	Atomic weight	Source of lead	Atomic weight
Commercial lead salt....	207.22	Cerrusite from Australia	207.22
Eifel Mts., Germany....	207.20	Galena from Missouri...	207.22
Cerrusite from Idaho....	207.21	Galena from Germany..	207.21
Vanadinite, Arizona.....	207.21	Galena, Washington....	207.21

out upon examining specimens from widely separated sources. Neither of these expectations was realized, and so far there is, therefore, no evidence that ordinary lead is a mixture.

"Lead" from *radioactive* minerals collected at widely separated points[1] has an atomic weight which is far from that of

TABLE 121.—ATOMIC WEIGHT OF RADIOACTIVE "LEAD"

Source of lead	Atomic weight
Norway clevite	206.08
North Carolina uraninite	206.40
Australian carnotite	206.38
Joachimsthal pitchblende	206.57
Colorado carnotite	206.59
Ceylon thorianite	206.82
English pitchblende	206.86
Colorado carnotite	207.00

ordinary lead, and different in different minerals, as may be seen in Table 121. The methods of purification were as carefully selected as in the case of ordinary lead above. Careful spectrum analysis showed the absence of impurities in the specimens of lead, and experimental errors large enough to account for this

[1] RICHARDS and LEMBERT, *J. Am. Chem. Soc.*, **36**, 1329 (1914); **38**, 2613 (1916). RICHARDS and HALL, **48**, 704 (1926).

difference are entirely out of the question, as the work was done with extreme care by experienced workers.

Finally,[1] a large quantity of radioactive lead (atomic weight 206.41) was converted into nitrate, and this was subjected to a series of fractional crystallizations such as are used to separate the rare-earth elements, until about a thousand fractionations had been performed. The most soluble and least soluble end portions showed no difference of atomic weight, and no difference in beta-ray activity; hence this number of crystallizations effected no separation.

The isotopes of lead have identical atomic volumes,[2] hence different densities; that of ordinary lead is 11.337 and that of radioactive lead 11.289 in one specimen and 11.273 in another (atomic weight 206.08). The molal solubilities are identical[3] for the nitrates of isotopes; their indices of refraction and their spectra are also identical.[4] No method of separating them has yet been found effective for lead, and we are, therefore, forced to conclude that elements which have different atomic weights may have identical chemical properties, such that the isotopic forms are absolutely inseparable; and that elements of different atomic weight must be assigned the same place in the periodic table.

Isotopes of Light Elements.[5]—Evidence of another sort has been obtained that many elements are isotopic, that is, contain *chemically identical* atoms of different weight. When the positive rays from a discharge tube are passed between charged plates, they are deflected toward the negative plate. By means of apparatus arranged as in Fig. 70, positive rays are sorted into an extremely thin ribbon on passing through the parallel slits S_1 and S_2, and are then spread into an electric "spectrum" by means of the charged plates P_1 and P_2, of which the latter is negative. A portion of this spectrum deflected through a given

[1] Richards and Hall, *J. Am. Chem. Soc.*, **39,** 531 (1917).

[2] Richards and Wadsworth, *J. Am. Chem. Soc.*, **38,** 1658 (1916).

[3] Richards and Schumb, *J. Am. Chem. Soc.*, **40,** 1409 (1918).

[4] Merton, (*Proc. Roy. Soc. London*, (*A*) **96,** 388 (1920)) and Harkins, (*J. Am. Chem. Soc.*, **42,** 1329 (1920)) claim to have found very slight differences in the spectra of isotopic forms of other elements.

[5] Aston, *Nature*, **104,** 393 (1919); **105,** 617 (1920); *Phil. Mag.*, **39,** 449 (1920); *Science Progress*, **15,** 212 (1921); *Phil. Mag.*, **47,** 385–400 (1924).

ngle is selected by the diaphragm D and passed between the ircular poles of a powerful electromagnet O, the field of which s such as to bend the rays back again through a greater angle han that of the first deflection. The result of this is that rays aving a constant mass (or more properly a constant ratio m/e f mass to charge) will converge to a focus at F and indicate heir position upon a photographic plate placed as shown, giving

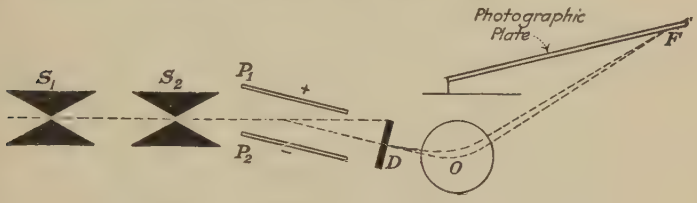


FIG. 70.—Positive-ray spectrograph.

"spectrum" dependent upon mass alone. On account of its nalogy to optical apparatus, the instrument is called a positive-ay spectrometer and the spectrum produced is known as a mass pectrum. A sketch of the spectrum obtained for neon is shown n Fig. 71. Displacement to the right with increasing mass is een to be approximately linear; the numbers indicate masses orresponding to O = 16. Only relative measurements are

FIG. 71.—Mass spectrum of neon.

btained, in terms of particles of known mass. These particles re impurities in the gas investigated, sometimes introduced urposely to aid in the smooth operation of a discharge tube. he principal groups of reference spots shown correspond to xygen 16, two lighter spots at 24 and 26 are probably C_2 and $_2H_2$, and the strong spot at 28 is C_2H_4 or CO. The two chief ots for neon are shown by careful comparative measurements n the actual photographic plates to be at 20.0 and 22.0, and ot at 20.2, which is the accepted atomic weight of neon. Neon herefore consists of a mixture of these two kinds of atoms, in he proportions of about 9 to 1.

In the same way magnesium, atomic weight 24.32, has been resolved in the positive-ray apparatus[1] into isotopes of atomic mass 24.0, 25.0, and 26.0. Other elements have also been resolved into isotopes, of which mercury contains perhaps 6. All of the isotopes so far encountered have atomic masses which are strictly whole numbers. A still more striking spectrum is that derived from chlorine, shown in Fig. 72. The strong spots at 28 and 44 are carbon monoxide and carbon dioxide, and a spot at 32 shows that a slight trace of oxygen is present. The spectrum of chlorine is characterized by four strong lines at 35.0, 36.0, 37.0, and 38.0; there is no trace of a line at 35.46, the accepted atomic weight of chlorine. The lines at 35.0 and 37.0

FIG. 72.—Mass spectrum of chlorine.

are due to chlorine atoms; the other lines one unit higher are their corresponding HCl compounds. This is strong evidence that chlorine consists of two isotopes whose atomic weights are whole numbers on the oxygen scale. Of course, these two chlorines are chemically identical in every way, and inseparable by chemical means, so that the practical chemistry of chlorine is not disturbed in any way. Since these atoms have different atomic weights, there may be three kinds of chlorine molecules of molecular weight 70, 71, and 72. Denoting the 35 chlorine by its usual symbol Cl and the 37 chlorine by Cl′, the possible molecules are Cl_2, Cl_2', and Cl.Cl′. Molecules of different mass diffuse at different rates (Graham's law of diffusion, page 49), and it is possible for a sufficiently large number of fractional diffusion experiments to yield two samples of chlorine gas of different densities. Harkins[2] reports that he has separated chlorine into fractions of atomic weight 35.515 and 35.418 by the fractional diffusion of gaseous hydrogen chloride.

Much research work has been done upon isotopes, and the results of it are summarized in an International Table of isotopes.[3]

[1] DEMPSTER, *Science*, **52**, 559 (1920).

[2] *J. Am. Chem. Soc.*, **43**, 1803 (1921); **48**, 58 (1926).

[3] *J. Am. Chem. Soc.*, **45**, 869 (1923). See also ASTON, "Isotopes," 2nd ed. (1924).

So far no element has been found to have a fractional atomic weight except hydrogen. If oxygen is assigned the atomic weight 16.00, helium is 4.00, and hydrogen 1.008, as shown by the positive-ray spectograph. No element of odd atomic number has yet been found to have more than two isotopes, and all elements in the list conform to the rule that elements of odd atomic number have odd atomic weights. V, Cr, Mn, Co, Sr, and Yt have no isotopes.[1]

Isotopes and the Law of Definite Proportions.—From the experiments upon the atomic weight of radioactive lead and ordinary lead, quoted above, it is clear that lead bromide contains a variable proportion of lead, according to whether ordinary or radioactive lead is concerned. These determinations of atomic weight were made from the percentage of bromine in lead bromide, as determined by precipitation of silver bromide. When isotopes are concerned, the composition of a chemical compound is a variable quantity. If it should happen that chlorine can be largely separated into fractions of different atomic weight, then chlorides may have variable compositions, according to which isotope is combined in the compound. The experiments of Aston with his positive-ray spectrograph indicate that other common elements are mixtures of isotopes.

This is not as serious as might at first appear. The positive-ray spectrograph has not yielded weighable quantities of the separate isotopes of chlorine, and enough work has been done upon their separation in quantity to show that it can be accomplished only with very great difficulty, and after long series of fractional diffusion experiments, or other laborious methods. Isotopes have *identical* chemical properties, they are absolutely inseparable by chemical means. The quantity of radioactive lead at present available is quite small, and the practical chemistry of lead is in no way affected. So far as practical everyday chemistry is concerned, the law of definite proportions is essentially unshaken, though in stating it a sort of mental reservation must be made for the compounds of radio-lead. No reservations are yet needed for chlorine compounds, for, while the positive ray spectrometer shows convincingly that chlorine consists of two isotopes, no case is known in which these isotopes

[1] ASTON, *Phil. Mag.*, **47**, 385 (1924).

have been found separated in nature. Much careful work on its atomic weight has led to results which show that chlorine as ordinarily encountered, from whatever source, or in whatever state of combination, behaves as an element of atomic weight 35.46; long experience has shown that it may be considered as an elementary substance. There is not the slightest probability that chlorine will be separated into its isotopes in sufficient quantity to influence its everyday chemistry, so long as this separation looks to fractional diffusion methods or to positive ray separation.

Age of Minerals.—If all of the lead in a mineral is assumed to be of radioactive origin, and all of it has come from the decay of uranium, then a calculation of the age of the mineral may be made from the known rate of decay of uranium. This calculation has often been made, and the results agree as to the order of magnitude, but it is quite uncertain that all lead in any mineral was so formed, and that no other alteration has taken place in a mineral in the enormous time interval involved. Most of such calculations lead to the order 10^9 years,[1] but the individual calculations of various authorities vary between 1×10^9 and 11×10^9.

Thorium Series.—In addition to the uranium series of radioactive changes already discussed, there is another series of which thorium is the parent element. The changes involved consist of the expulsion of alpha and beta particles, with corresponding losses in atomic weight when the former are lost, and with the corresponding shifts in position of the elements in the periodic table. The end product of this series is isotopic with ordinary lead, just as is the end product of the uranium series; it is formed from thorium (atomic weight 232.1) with the loss of six helium atoms, and should therefore have an atomic weight 24 units less than thorium, or 208.1. It will be noted that this is higher than the atomic weight of ordinary lead, while the end product in the uranium series has an atomic weight lower than ordinary lead. It is possible that ordinary lead is a mixture of these two inactive end products, always in constant proportion, but this is exceedingly unlikely in view of the work on the atomic weight of inactive lead from widely separated sources mentioned above. In all

[1] See F. W. Clarke, *Proc. Nat. Acad. Sci.*, **4**, 181 (1918).

of the specimens of inactive lead there examined, none had an atomic weight deviating by more than 0.01 unit from the average. Perhaps there are three leads, an inactive one (ordinary lead) and the two active end products.[1] At least a specimen of lead thought to have come from thorium disintegration has shown an atomic weight of 207.90, which is higher than that of ordinary lead,[2] but which cannot be the pure end product, since this should have the atomic weight 208.1.

Actinium Series.—This third series contains no elements of long life, and has the same general characteristics as the others already described. It need not be given in detail here.

References.—Details of the fascinating topics given briefly in this chapter should be sought in the original papers quoted. The following textbooks are also recommended: FAJANS, K., "Radio Activity," translated from 4th German ed. (1922). SODDY, F., "Interpretation of Radium" (1922). RUTHERFORD, E., "Radioactive Substances and Their Radiation," *Nat. Research Council, Bull.* **10,** No. 51 (1925).

[1] CLARKE, *Proc. Nat. Acad. Sci.*, **4,** 181 (1918).
[2] HÖNIGSCHMID, *Physik. Z.*, **19,** 436 (1918).

CHAPTER XIV

ATOMIC STRUCTURE

We have seen in earlier chapters that the distance between atomic centers in liquids and solids is of the order 10^{-8} cm., or about a thousandth of the shortest wave length of visible light. It is, therefore, clear that any evidence of the internal structure of such a particle is necessarily indirect. Indeed, it seems almost impossible that anything at all could be known of such an exceedingly tiny particle. Not many years ago, mention of the chemical analysis of stars and planets would have seemed so far removed from possibility; yet this has been accomplished through their spectra, and one element (helium) was shown to be present in the sun before it was discovered on the earth. The elucidation of atomic structure is not more remarkable.

Evidence Already Presented.—From consideration of the periodic table it seems probable that something within the atom which is responsible for many of its chemical properties is repeated every eighth element. In attempting to visualize its structure, it is therefore necessary to have a similar arrangement within the atom every eighth element when they are arranged in the order of increasing atomic numbers. We have seen from the phenomena of radioactivity that helium atoms are expelled from heavy metal atoms during atomic disintegration of one type, and that negative charges are expelled in another type of radioactive change; hence these must form the fundamental constituents of these atoms, and presumably of the more stable atoms as well. There are eight radioactive transformations in which helium atoms are expelled in the uranium series, six in the thorium series, and five in the actinium series. The probability that helium is one of the units of atomic structure in other atoms as well as those involved in radioactivity is strengthened by the fact that the atomic weights of a number of elements differ by exactly four units.

The fact that the helium nucleus survives the violent expulsion from a radioactive atom suggests that it is a very stable unit. A substance which breaks up with the emission of swiftly moving electrons (beta particles) follows the same laws as one which gives out helium atoms. It is probable that these electrons also come from the same part of the exploding atom, and that they are constituents of the complex atom in the same way that the helium atoms are. The atoms of elements are not electrically charged when in the free state; hence there must be an equal number of positive and negative charges in them.

Two simple possibilities present themselves. Either all of the positive electricity is on the outside of the atom and the negative electricity within it; or the positive electricity is concentrated in the interior of the atom and the negative electric charges are on the outside. It is certain that positive electricity is to be found associated with the mass of the atom in either case, for positive electric charges having no appreciable mass have never been observed. Electrons (negative charges) do exist without association with matter of any kind; they are in effect massless "atoms" of electricity; no corresponding positive electron is known.

Scattering of Alpha Particles by Matter.[1]—When a beam of swiftly moving alpha particles is passed through gold, an occasional particle is deflected through an angle greater than a right angle, presumably on account of having entered into the very core of an atom and there encountered an intense electric field. In order to account for the intensity of this field it is necessary to suppose that the positive electricity is concentrated in a very minute volume (compared to the distance between atoms), or nucleus. The field which could come from a uniform distribution of the positive electricity around a sphere 10^{-8} cm. in diameter is far from strong enough to explain the observed deflections of alpha particles.

Rutherford Atom Model.—It is now commonly accepted that an atom consists of a small positive nucleus with which is associated the mass of the atom, and a system of electrons which

[1] GEIGER and MARSDEN, *Proc. Roy. Soc. London*, (*A*) **82**, 495 (1909); *Phil. Mag.*, **21**, 669 (1911); **27**, 488 (1914); see also RUTHERFORD, *Proc. Roy. Soc. London*, (*A*) **97**, 378 (1920).

form the outer layer of it. The material in the following pages relates, first, to the structure and diameter of this inner mass nucleus; second, to the number and arrangement of the outer electrons, and the relation of this arrangement to chemical behavior. Evidence bearing on both topics is of necessity indirect or circumstantial; much of it is mere plausible speculation, but it is worthy of attention and study, for it points the way to future research and serves as a working basis in present problems. A nuclear structure was first proposed by Rutherford,[1] and such a model is often called after him.

Atomic Number.—In the previous chapter it was stated that when the elements were arranged in the order of increasing atomic weight (after such irregularities as the positions of argon and potassium, tellurium and iodine, etc. were eliminated by placing these elements in their proper columns), the order number of each element was called its atomic number. Except for the evidence based on characteristic X-ray frequency, there was nothing to indicate that the atomic number was anything more than the order number, arbitrarily changed in two or three cases to make the periodic table more systematic. If we define the atomic number of an element as the *number of positive charges on its nucleus*, as determined in experiments on atomic structure, the same order is obtained as in the periodic system. In fact, there is a simple relation between atomic number and the frequency of characteristic X-ray spectra, as determined by Moseley's experiments mentioned in the previous chapter. If n is the atomic number as defined above (magnitude of the positive charge on the nucleus of an atom), and f is the frequency of vibration,

$$f = a(n - b)^2,$$

where a and b are constants. The elements when arranged according to the atomic numbers thus determined fall into their proper places in the periodic table. Hence the atomic number of an element is a more fundamental property of it than its weight. *The atomic number of an element is the number of positive charges on its nucleus.* These atomic numbers are also deduced from scattering of X-rays on passing through matter, and from the

[1] *Phil. Mag.*, **21**, 669 (1911); **26**, 702 (1913); **27**, 488 (1914).

scattering of alpha particles, the same number being obtained by any of the methods.

Structure of Atomic Nuclei.[1]—From the closeness of the low atomic weights to whole numbers if oxygen is 16.000, and from the relative abundance in the earth's crust of elements of even atomic number, a theory has been postulated as to the origin of elementary atoms,[2] which assumes their nuclei to be built up from alpha particles (positively charged helium atoms), positively charged hydrogen atoms, and electrons, the latter not contributing to the mass of an atom to an appreciable extent. Those elements whose atomic weights are divisible by 4 (carbon, oxygen, neon, magnesium silicon, sulfur, etc.) are considered as built up of a nucleus containing the required number of helium nuclei to give the proper weight; thus $3He^{++}$ for carbon, $4He^{++}$ for oxygen, $5He^{++}$ for neon, etc., plus a system of electrons in a shell surrounding the atom, such that the atom as a whole is electrically neutral. On account of the great stability of helium, these atoms of even atomic number, which are supposed to contain helium only, should be more stable than those of odd atomic

[1] The student of chemical history will recognize in the speculations of this paragraph a modification of Prout's hypothesis (1834) that the atomic weights were exact multiples of that of hydrogen. The underlying thought of this hypothesis is a building up of elements from hydrogen as a fundamental constituent of all matter. Clarke long ago (1873) postulated an evolution of elements, and this has been supported in late years by spectroscopic observation of the planets. Lockyer and others have pointed out that the spectra of hydrogen and helium predominate in the hot stars. Evolution of elements is indicated by a progressive increase in chemical complexity of the heavenly bodies as their temperatures decrease from those of the simple gaseous nebulæ to the sun and colder planets like the earth. The more complex (heavier) elements do not appear until lower temperatures are reached. The spectrum lines of lead appear in the solar spectrum, while those of uranium and thorium do not appear. Against this plausible argument must be set the facts of radioactivity; namely, that uranium and thorium do break up their atoms spontaneously, with the formation of an end product chemically identical with lead. Here we are able to observe an uncontrolled and spontaneous disintegration of atoms; no synthesis of atoms of any kind has been observed, though the spectra of stars indicate the possibility that it does take place at exceedingly high temperatures. See CLARKE, *Proc. Nat. Acad. Sci.*, **4**, 181 (1918).

[2] HARKINS, *Science*, **50**, 577 (1919); *Nature*, **105**, 230 (1920); *Phys. Rev.*, **15**, 73 (1920); *J. Am. Chem. Soc.*, **39**, 856 (1917); **42**, 1956 (1920); see also MCLENNAN, *Science*, **55**, 219 (1922).

number, which are supposed to contain hydrogen in their structure. There is no direct test of the stability of any of the non-radioactive elements, since they are unchangeable by all physical and chemical means within our power, but if they were really built up in the way here postulated, the more stable ones should be more abundant in the universe. Meteorites contain about 99 per cent of elements of even atomic number; the earth's crust contains about 90 per cent of these elements. Direct proof of this bold hypothesis has not, of course, been accomplished, but the circumstantial evidence in its favor commands attention. In order to account for the fact that the effective mass of hydrogen atoms in other nuclei is 1.000 and not 1.0076, Harkins assumes a change of mass[1] which he calls the packing effect. This assumption is not particularly reasonable, since he assumes it for hydrogen and not for helium. Thus he supposes that the reaction 4He = O occurs without loss of mass, but that 3He + 2H = N requires a decrease of mass and He + 3H = Li requires one. This would seem to imply a greater stability for the elements presumed to contain hydrogen, and it is the contrary which he assumes and which the facts quoted seem to support. His speculations are borne out by the greater abundance of elements whose atomic weights are divisible by 4, and which he presumes to contain helium only. With the discovery of hafnium (element 72) all of the elements of even atomic number become known, and the three undiscovered elements all have odd numbers, 61, 85, and 87.

Heavy elements do actually give off helium during their radioactive changes. Hydrogen seems to have been obtained as a result of extremely violent bombardment of nitrogen molecules with alpha particles (charged helium atoms) of exceedingly high velocity,[2] while no hydrogen was obtained from similar

[1] According to the theory of relativity, mass may be changed into energy. When the reaction 4H = He takes place, there is a decrease of mass of 0.030 gram, since 4 atomic weights of hydrogen weigh 4.030 grams and the resulting helium weighs 4.00 grams. This loss of mass corresponds to 0.030 $(3 \times 10^{10})^2$ c.g.s. units or 65×10^{10} cal. per atomic weight of helium formed. Hence this quantity of energy would be required to decompose a mol of helium into hydrogen, and it is not remarkable that its decomposition by artificial means has not been accomplished.

[2] Rutherford, *Phil. Mag.*, **37**, 571 (1919); *Science* **50**, 467 (1919); *Proc. Roy. Soc. London*, (*A*) **97**, 374 (1920).

bombardment of oxygen molecules. Harkins' hypothesis states that the nitrogen nucleus contains hydrogen and that the oxygen nucleus contains none; and this remarkable experiment by Rutherford thus seems to be a confirmation of Harkins' views.

Following this line of speculation further, a new periodic table (Table 122) has been prepared which shows the structure of each atomic nucleus and the agreement between the atomic weight calculated on the assumption of such a nuclear structure with that based on the usual methods of determining atomic weights. This system of representing atomic structure fails after the third period of the table, and atomic weights which are not close to whole numbers are more common from this point on. In the first 28 elements there are cases in which the atomic weights are not close to those demanded by this hypothesis. In many of these cases it has been shown by other investigators[1] from the deflection of charged atoms or positive rays in a powerful electric field that the element consists of two isotopes of different atomic weight. Thus neon and chlorine are assigned only one arrangement for the nucleus, but the isotopes have different masses and should be considered separately in view of this more recent knowledge.

In connection with this table, it should be noted that the increment in weight between the first series of elements (helium to fluorine) and the second series (neon to chlorine) is 16, or 4He, the increment from this series to the following one is 5He, and the increment to the next series, not shown in the table, is 6He. This increment persists even in the elements of odd atomic weight, such as lithium, boron, and fluorine. There is an unexplained exception in the increase in weight from nitrogen to phosphorus, which is 17 in place of 16, and other exceptions occur with increasing frequency for elements of higher atomic weight. This indicates that there is some other law yet to be discovered which regulates these increases. If the actual atomic weights of the elements supposed to consist of helium nuclei only are divided by the number of such nuclei present,[2] values for the atomic weight of helium are obtained as shown in Table 123.

[1] Aston, *Nature*, **104**, 393 (1919); Dempster, *Science*, **52**, 559 (1920).

[2] Harkins, *J. Am. Chem. Soc.*, **42**, 1988 (1920).

TABLE 122.—HYDROGEN-HELIUM STRUCTURE OF ATOMS (ACCORDING TO HARKINS)

	Even group 0	Odd group 1	Even group 2	Odd group 3	Even group 4	Odd group 5	Even group 6	Odd group 7
Atomic number	2	3	4	5	6	7	8	9
Element	He	Li	Be	B	C	N	O	F
Atomic structure	He	$He + H_3$	$2He + H$	$2He + H_3$	3He	$3He + H_2$	4He	$4He + H_3$
Calculated atomic weight	4.0	7.00	9.00	11.0	12.0	14.00	16.00	19.00
Determined atomic weight	4.0	6.94	9.10	10.9	12.0	14.01	16.00	19.0
Atomic number	10	11	12	13	14	15	16	17
Element	Ne	Na	Mg	Al	Si	P	S	Cl
Atomic structure	5He	$5He + H_3$	6He	$6He + H_3$	7He	$7He + H_3$	8He	$8He + H_3$
Calculated atomic weight	20.0	23.00	24.00	27.0	28.0	31.00	32.00	35.00
Determined atomic weight	20.2	23.00	24.32	27.1	28.3	31.04	32.06	35.46
Atomic number	18	19	20	21	22	23	24	25
Element	A	K	Ca	Sc	Ti	V	Cr	Mn
Atomic structure	10He	$9He + H_3$	10He	11He	12He	$12He + H_3$	13He	$13He + H_3$
Calculated atomic weight	40.0	39.00	40.00	44.0	48.0	51.00	52.00	55.00
Determined atomic weight	39.9	39.10	40.07	45.1	48.1	51.0	52.0	54.93

The author of this hypothesis of atomic structure considers that he has good reason for omitting from consideration the elements in Table 123 which are enclosed in parentheses. The strength of his theory is much weakened by the fact that he does not find any reason for omitting an element whose atomic weight is an exact multiple of 4, but does discard magnesium and silicon, which consist of isotopes. There can be little doubt, however, that some truth underlies these speculations; radioactive changes show that helium is beyond question a constituent of the heavier atoms, and it would be strange if it were not in the nucleus of lighter atoms as well.

TABLE 123

Element	Number of helium nuclei	Atomic weight of helium	Element	Number of helium nuclei	Atomic weight of helium
Carbon	3	4.001	Titanium	12	4.008
Oxygen	4	4.000	Chromium	13	4.000
(Neon)	5	(4.040)	Iron	14	3.989
(Magnesium)	6	(4.050)	Thorium	58	4.003
(Silicon)	7	(4.045)	Uranium	59	4.003
Sulfur	8	4.008	Radium	56	3.998
Argon	10	3.990	Radio-lead	51	4.001
Calcium	10	4.007			

Number and Arrangement of Electrons in Atoms.—If the atomic number is the number of positive charges on an atomic nucleus, it is also the number of electrons entering into an atomic structure, since atoms as a whole are electrically neutral. These electrons are sometimes assumed to rotate around the atom[1,2,3] in closed orbits, and to pass from one orbit to another in such a way as to give rise to the characteristic spectra. When an element contains several electrons which rotate simultaneously about its nucleus in various orbits, the treatment necessarily becomes very complicated. We shall return to a consideration of this type of atom model in a later paragraph. A more important objection to this idea is that it does not bring about a repeti-

[1] BOHR, *Phil. Mag.*, **26**, 1, 477, 857 (1913); **30**, 394 (1915).
[2] NICHOLSON, *Phil. Mag.*, **27**, 541 (1914); **28**, 90 (1914).
[3] KOSSEL, *Ber. deut. physik. Ges.*, **16**, 953 (1914).

tion of any arrangement every eighth element as it should to account for the periodic table. Many have given more weight to an assumption that the electrons associated with an atomic nucleus are more or less stationary, and vibrate only within a range which is narrow compared to the atomic diameter. Since the recurrence of properties comes every eighth element, it is natural to assume that the electrons occupy nearly stationary positions at the corners of an imaginary cube circumscribed about the atomic nucleus.[1] The existence of isotopic elements having identical chemical properties and different atomic weights, and therefore different nuclear structures as well, clearly shows that the nucleus does not determine the chemical properties of elements. It is natural to seek the explanation in the arrangement of electrons, for that reason. Let us consider a few simple elements in detail.

Hydrogen and Helium.—A hydrogen atom has but one electron, helium has two which are supposed to be situated on opposite sides of the atomic nucleus. This arrangement of electrons is probably the most stable of any, and helium is probably the most stable element. Two hydrogen atoms combine to form a molecule, their electrons forming a stable pair. These elements are not considered in the cubical arrangement, which begins with lithium.

Lithium to Neon.—Lithium has three electrons and three positive charges upon its nucleus. Two electrons are assumed to be within the cube, forming a pair such as that in a helium atom or a hydrogen molecule, but this pair is not shown in drawing the diagrams. This is also the case in all of the following

[1] This idea was apparently first proposed by Parson, *Smithsonian Inst. Misc. Pub.*, **65,** 11 (1915); clarified and elaborated by G. N. Lewis, *J. Am. Chem. Soc.*, **38,** 762 (1916); and finally widely extended by Langmuir, *J. Am. Chem. Soc.*, **41,** 868, 1543 (1919); **42,** 274 (1920); *J. Ind. Eng. Chem.*, **12,** 386 (1920). Similar views have been expressed by Wyckoff, *J. Wash. Acad. Sci.*, **9,** 565 (1919); Kossel, *Naturwissenschaften*, **7,** 339 (1919); Kirchoff, *Z. physik. Chem.*, **93,** 623 (1919), and others. In the treatment here given, no attempt is made to credit the various writers with their share in formulating this theory; and only the essential features are considered at all. Many of the interesting consequences of this work are available to elementary students who care to study the original papers, especially those of Lewis and Langmuir.

elements. The third electron in lithium, the third and fourth in beryllium, etc. have the positions shown[1] in Fig. 73.

It is assumed that every element having an incomplete set of eight electrons, an "octet" of electrons around it, tends to complete this octet if it is nearly full already, or to give up its electrons to complete the octet of another element in case it has few of them. Thus lithium has no tendency to take on seven other electrons to complete its octet, but readily gives up its one electron to complete the octet of fluorine. The chemical union of lithium with fluorine is thought to consist of this transfer of an electron. After it has taken place, the lithium atom would

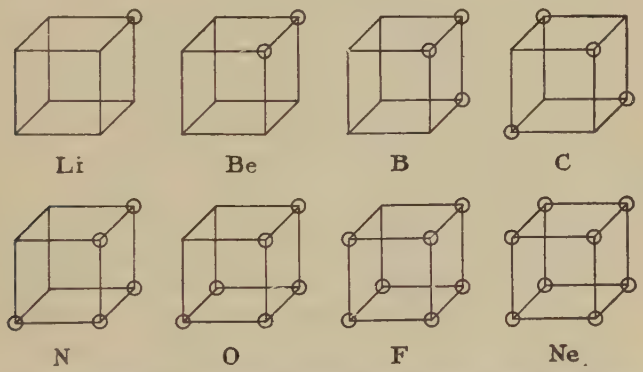


FIG. 73.—Arrangement of electrons around the atomic nuclei for elements in the first period of the periodic table. (*After Lewis.*)

be positively charged, since it has lost one outer electron but still retains its three unit positive charges on the nucleus, corresponding to 3 as its atomic number, and the two electrons which form the stable pair of the helium conformation. Thus the crystal lattice of lithium fluoride and of the other alkali halides may well consist of the *ions* of lithium fluoride. If this is true, the formation of ions when the crystal forces are released by dissolving the salt in water is not a surprising consequence, nor would one be surprised if ionization were complete. However, similar considerations apply to hydrogen fluoride, and its ionization in solution is certainly far from complete.

[1] Photographs of space models of these and other atoms are given by FOSTER in *Chem. Met. Eng.*, **23**, 690 (1920).

Neon, having a complete octet of its own, neither gives up electrons to any other element or takes on any from another element, and hence it forms no compounds. Berylium has two electrons, and can give one of them to each of two fluorine atoms, thus completing two octets; and this is in agreement with the formula BeF_2 for this compound. But berylium has no tendency to combine with lithium, since no octets could be completed by such a combination. Now the electron shell of oxygen lacks two electrons of a complete octet, and these may be taken from two lithium atoms (forming Li_2O) or from one berylium atom (BeO). The electron shell of carbon lacks four electrons of being complete, it may give up two electrons to each of two oxygen atoms to complete their octets (forming CO_2), or it may take up four electrons from four hydrogen atoms to complete its own octet (CH_4). This is the first element which can either complete its own octet or give all of its electrons to another atom or group of atoms.

Sharing Electrons.—When an element is not afforded an opportunity to complete its octet at the expense of some other atom or atoms, it may share a pair of electrons with another atom of its own kind. That is, two fluorine atoms may combine as shown in Fig. 74, if their octets have two electrons which exist in both octets at once. This explains the existence of a very stable molecule F_2. But this arrangement is less satisfactory, and less stable, than eight electrons for each octet. Hence this arrangement is readily abandoned in the presence of such elements as hydrogen or lithium which will give up an electron. It is generally true that chemical combination will take place by completing octets if possible, and by sharing pairs of electrons as second choice. The oxygen molecule is formed so as to contain two completed octets in which two pairs of electrons are shared, corresponding to two edges of the cube being in contact.

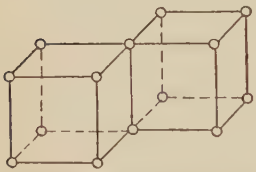


FIG. 74.—Electron arrangement in a fluorine molecule.

Sodium to Argon.—(Second period of the periodic table.) The first element after neon is sodium, which must have an electron arrangement similar to lithium if this is responsible

for the chemical properties. The inner stable pair is completed; the first octet is completed, and one electron is available for beginning a new octet outside of the first one. There appears to be no tendency for the 10 electrons of the stable pair and the first octet to exert any effect upon the properties of sodium; they remain undisturbed by chemical processes, and only the single electron of the outside octet is active. This is apparently true of all the elements; their chemical properties depend almost completely on the outside layer of electrons, not upon the inner layers, and no element starts to form a second octet until the octet under it is completely filled. Sodium has eleven electrons, two for the stable helium conformation, eight for the stable neon octet, and one in the new octet. It has no capacity for taking on seven other electrons, but readily gives up one to complete the octet of another element. Having lost this electron, it has 10 negative electrons and 11 positive charges in its nucleus; it is therefore positively charged, and such a structure is found in the free sodium ion in solution. Langmuir believes that this sodium ion also exists in the solid crystal, and that the chlorine atom has taken an electron into its octet from sodium even in a salt crystal, which consists of the *ions* held in a space lattice.

Magnesium has an arangement of electrons in the outer shell like berylium, aluminum like boron, and silicon like carbon, so far as the *outside* shell of electrons is concerned, and it is mainly this outside layer which governs the chemical properties of atoms. In silicon there is the tendency to give up four electrons as in $SiCl_4$ or to take up four electrons as in SiH_4, and the following elements, phosphorus, sulfur, and chlorine, show a decreasing tendency to give up five, six, or seven electrons, together with an increasing tendency to take on three, two, or one and complete their own octets. Chlorine has 17 electrons, and by taking on one more, as in a combination with lithium or sodium, it completes its second octet and has the electron arrangement of argon. As in the case of fluorine, chlorine will share a pair of electrons with another chlorine atom; the electron arrangement in the outer shell of a chlorine molecule is the same as that shown in Fig. 74 for fluorine. In the simplest oxide of chlorine, oxygen (which lacks two electrons of completing its first octet) may share two pairs of electrons with two chlorine atoms, thus completing

three octets in which certain electrons are forced to share in two octets at once. The arrangement is shown in Fig. 75.

Continuing through the elements after argon, the first three, potassium, calcium, and scandium, seem to follow along the same system as in the first two periods; potassium behaves much like sodium, calcium like magnesium, etc. But with the twenty-second element, titanium, some new set of influences seems to begin. Titanium is not like carbon or silicon, vanadium has properties widely different from phosphorus, chromium does not resemble sulfur in as many ways as it differs from it, and manganese bears little resemblance to chlorine. In all of these cases, there is some resemblance between elements in the columns of the periodic table, but there is more difference. The authors of

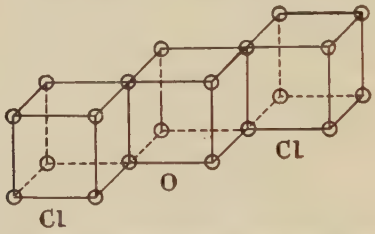


Fig. 75.—Electron arrangement in chlorine monoxide.

this hypothesis of electron arrangement have not yet carried their speculations much beyond calcium, and we shall not attempt to do so. Let us examine some of the consequences of the electron structures assigned to the first 20 elements, especially in their bearing on the physical properties of compounds in which the electron arrangement is similar. We have seen already that elements of similar chemical properties have similar electron arrangements, and that the maximum number of electrons in an outer shell is eight, thus accounting for the periodic system.

Physical Properties and Electron Arrangement.—Let us take for comparison two molecules in which the total number of electrons is the same, and which according to this theory have the same structure so far as arrangement of electrons is concerned. Nitrous oxide and carbon dioxide each contain 16 electrons; each molecule is formed by the sharing of electrons in such a way that a central atom shares four pair of electrons, two pairs with each

of the adjacent octets. The arrangement is shown in Fig. 76. Each molecule contains three atomic nuclei, and there is thus great probability that their physical properties should be much alike *if the theory is correct.* There is not much other ground for expecting similarity except that their molecular weights are

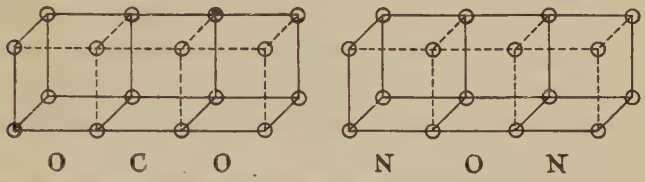


FIG. 76.—Electron arrangements of carbon dioxide and nitrous oxide.

equal, and in other cases this is not found to bring about much resemblance of properties. Table 124 shows that there is great resemblance in physical properties of these two substances. Two other molecules of quite different chemical nature have also been found to have similar physical properties, nitrogen and carbon

TABLE 124.—COMPARISON OF PHYSICAL PROPERTIES[1]

Property	N_2O	CO_2
Critical pressures	75 atm.	77 atm.
Critical temperatures	35.4°	31.9°
Viscosity at 20°C	148×10^{-6}	148×10^{-6}
Heat conductivity at 100°C	0.0506	0.0506
Density of liquid at −20°	0.996	1.031
Density of liquid at +10°	0.856	0.858
Refractive index of liquid. D line, 16°C	1.193	1.190
Dielectric constant of liquid at 0°	1.598	1.582
Magnetic susceptibility of gas at 40 atm. 16°C	0.12×10^{-6}	0.12×10^{-6}

monoxide; and to have identical electron arrangements within the molecule, according to this theory.

Isosterism.[2]—Atoms or atomic groups having within them the same number and arrangement of electrons are called "isosteres." Thus neon, sodium ion, and magnesium ion are isosteric; the first having a complete outer octet, the second having

[1] LANGMUIR, *Proc. Nat. Acad. Sci.*, **5**, 258 (1919).
[2] LANGMUIR, *J. Am. Chem. Soc.*, **41**, 1548 (1919).

reverted to this form by the loss of its one electron to some other element, and the third by the loss of two outer electrons. Similarly, nitrate ions and carbonate ions, while their structures are somewhat complicated, having the same electron arrangement. Hence sodium nitrate and magnesium carbonate have the same electron arrangement, and it has been found that their crystallographic properties are identical.

Bohr's Atom Model.—Bohr's atom model resembles Rutherford's in assuming a small nucleus with a net positive electric charge, surrounded by one or more negative electrons. These electrons rotate around the nucleus in orbits in a manner similar to the rotation of the moon around the earth. The hydrogen atom, which is the simplest, consists of a single positive charge of electricity with which is associated practically all the mass, and a negative electron, which rotates around the nucleus with great velocity. The basic principles of this atom model are the laws of electrostatic attraction and Newton's law of motion. There are two forces acting on an electron moving in an orbit: the electrostatic attraction tending to pull the electron toward the nucleus, and the centrifugal force due to its velocity in the orbit.

The normal configuration of the hydrogen atom is that in which the orbit of the electron is very close to the nucleus; it is the most stable configuration of a positive nucleus and a negative electron. As the electron approaches the nucleus, it loses potential energy and gains a smaller amount of kinetic energy. The atom as a whole loses energy and this is emitted in the form of light of definite wave lengths.

The unique assumption regarding this atom model is the existence of certain *definite* orbits. Thus when an electron drops from an outer orbit to an orbit closer to the nucleus, the emitted light, caused by the energy loss of the atom as a whole, is of one single frequency of vibration, a single atom can absorb only one single frequency of vibration of light at a time, corresponding to lifting the electron from an inner orbit to an orbit further from the nucleus. The hydrogen atoms collectively can absorb or emit a number of different single or monochromatic frequencies of light. These are called absorption or emission spectrum lines, and they have been classified into series. For example, the

Lyman *emission* series for hydrogen corresponds to the series of frequencies of light caused by an electron jumping from the outer orbits to the innermost orbit, which may be called orbit No. 1. The Lyman *absorption* series corresponds to the frequencies of vibration of light which will cause the electron to jump from

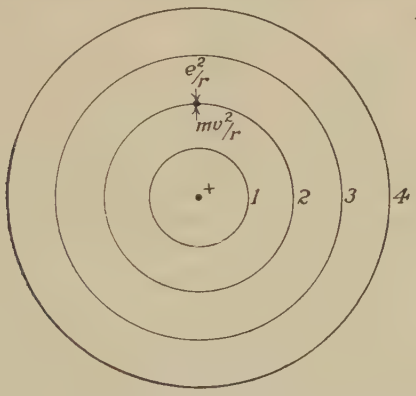


FIG. 77.—Orbits of the electron around a hydrogen nucleus.

orbit No. 1 to orbit No. 2 or 3 or 4, etc. In fact, there is a frequency of vibration of light which will cause the removal of an electron to the infinite orbit, which corresponds to complete ejection.

The equation which relates ν, the frequency of vibration of the light, to the numbers of the initial and final orbits for emission of light is Rydberg's formula

$$\nu = k\left(\frac{1}{n^2} - \frac{1}{n'^2}\right),$$

where n is the number of the inner orbit and n' is the number of the outer orbit in a given jump.

TABLE 125.—SERIES IN THE SPECTRUM OF HYDROGEN

	n	n'	Region of spectra
Lyman series	1	2, 3, 4, 5, 6, etc.	Ultra-violet
Balmer series	2	3, 4, 5, 6, 7, etc	Visible
Paschen series	3	4, 5, 6, 7, 8	Infra-red

Other series are the Balmer and the Paschen series, which are described in Table 125.

Bohr's model for the simple hydrogen atom permits him to calculate the values for the frequencies in the Lyman, Balmer, and Paschen series within 0.1 per cent. This is considered one of the greatest feats of modern physics. Bohr has extended the reasoning based on the hydrogen model to explain other types of spectra, including the optical and X-ray spectra of the chemical elements.

References.—Readers who wish to make a careful study of the topics in this chapter are referred to the excellent book by ANDRADE, "The Structure of the Atom," Harcourt, Brace & Co., 1923. This book contains a remarkably clear presentation of the material bearing on atomic structure.

Reviews of the subject of atomic structure have been written from time to time. Some of the most readily accessible ones are as follows:

EVE, A. S., *Science*, **40,** 115 (1914).

THOMPSON, J. J., *Sci. Am. Suppl.*, **85,** 290, 306, 326, 346 (1918).

HARKINS and WILSON, *J. Am. Chem. Soc.*, **37,** 1396 (1915).

RUTHERFORD, E., *Smithsonian Inst. Rept.*, **1915,** 167–202.

DUSHMAN, S., *Gen. Elec. Rev.*, **20,** 186, 397 (1917).

RUTHERFORD, E., *Proc. Roy. Soc. London*, March, 1914; *A* **97,** 1956 (1920).

FAJANS, K., *Sci. Am. Supplement*, **81,** 82, 102 (1916).

DARWIN, *Nature*, **106,** 51, 81, 116 (1920).

Papers on specific portions of the general problem of atomic structure, giving details, are generally difficult reading for beginners, but they are exceedingly helpful in obtaining a grasp of the subject. The following may be read with profit, even though some of the matter in them is not thoroughly understood after several readings of the text.

LEWIS, G. N., *J. Am. Chem. Soc.*, **38,** 762 (1916).

HARKINS, *Phys. Rev.*, **15,** 73 (1920), and earlier papers.

LANGMUIR, *J. Am. Chem. Soc.*, **41,** 868, 1543 (1919); **42,** 274 (1920).

WYCKOFF, *J. Wash. Acad. Sci.*, **9,** 565 (1919).

SODDY, *Chem. News*, **107,** 97 (1913); *Nature*, **91,** 57; **92,** 399, 452 (1915).

CHAPTER XV

COLLOIDS. SURFACE CHEMISTRY

General.—The name "colloid" was first employed by Graham in 1861 to distinguish a certain class of substances from others which formed crystals more or less readily, and which he therefore termed crystalloids. Graham's colloids were substances which would not diffuse through a membrane. The term as now used includes all systems in which one phase is finely dispersed in another, but in which the dispersion falls significantly short of the molecular dispersion which is characteristic of true solution. Such systems may be divided roughly into two classes which are fairly well represented by suspensions and jellies; or suspensoids and emulsoids; or sols and gels, as they are commonly called. In the first class are such mixtures as smoke and clouds (suspensions of solids or liquids in air), many dye solutions, turbid liquids, and suspensions in general; in the second are most emulsions, jellies, such as silicic acid, agar, gelatin, gum arabic, etc.

Suspensoids.—These consist of particles which are (usually) too small to be seen under a high-power microscope, and which do not settle out upon long standing; to the unaided eye the finest suspensions appear perfectly homogeneous, and many others may have a faint milky appearance. It will be seen from this general statement that a sharp distinction between true solutions and colloidal suspensions has not been made. Indeed, the solutions of very large molecules, such as dye stuffs, behave in many ways like colloidal suspensions, and colloidal suspensions have some of the properties of dilute solutions. The suspensions commonly encountered are, of course, composed of substances insoluble in the dispersing liquid; thus gold, platinum, ferric hydroxide, arsenious sulfide, vanadium oxide, sulfur, alumina, chromium hydroxide, silver iodide, prussian blue, and similar substance form *hydrosols*, or aqueous suspensoids. As these substances are not absolutely insoluble in water, it will be under-

stood that the suspending medium or dispersion medium is really a saturated solution of the substances in question, but this saturated solution differs but little from pure water.

Degree of Dispersion.—The diameter of particles concerned in suspensoid formation depends upon the method of preparation; thus gold suspensoids may be red, purple, violet, or black, according to the average size of particle produced, though the color also depends upon the concentration of colloid and its method of preparation. A red gold sol usually results from reducing a dilute gold chloride solution with carbon monoxide or with formaldehyde; and a blue sol from reduction with hydrazine, but either color may be obtained by either method. Tannic acid usually gives red sols, but may give blue; and either color can be prepared by striking an electric arc between gold wires under water, depending again upon experimental conditions, concentration of dispersoid produced, etc. Generally, the red sols consist of smaller particles and the blue sols of larger ones. The actual diameter is best determined by counting the particles in a known volume of solution (by a method to be described presently), then evaporating a portion of sol and weighing the resulting deposit. From the number of particles per cubic centimeter, their weight, and the density of the dispersed substance, the average diameter is readily calculated. It should be borne in mind that diameters of individual particles in a sol may be very much larger and very much smaller than an average thus determined unless special precautions are taken to insure a nearly uniform size. This is accomplished by fractional setting, usually with the aid of a powerful centrifuge, or by the use of selective filters, called ultra-filters.[1] Diameters of particles can also be obtained from the density distribution of a sol under the influence of gravity, and in another way which will be described in connection with Brownian movement in a later paragraph.

Surface Phenomena.—According to Langmuir's theory of the structure of a solid, outlined on page 123, an atom within a solid exerts its chemical attraction in all directions; an atom in a surface has unsatisfied attraction or chemical affinity reaching out into space, for a distance comparable with an atomic diameter at least, and this attraction may bring about condensation of

[1] Bechhold, *Z. physik. Chem.*, **64**, 328 (1908).

molecules upon a surface. Adsorbed films of gases on glass are so explained. In a dispersed solid, such as the solid phase of a suspensoid, a very large surface per unit weight of substance is exposed to the surrounding liquid. It is, therefore, to be expected that suspensoids will exhibit adsorptive power to an increased extent, that they will attract and hold whatever molecules may be dissolved in the dispersing liquid, and that the properties of these colloids will be greatly influenced by this adsorption. It should be remembered, however, that the colloidal particles in the very finest sols are of the order of 10^{-6} cm. in diameter, while molecular diameters are of the order 10^{-8} cm., so that there are still some millions of molecules in the finest particles. Extent of surface is, therefore, of more importance than its curvature so far as adsorption is concerned.

Dialysis.—It is readily demonstrated that suspensoids consist of particles which are much larger than ordinary dissolved molecules by placing them in vessels of parchment paper, thin collodion, animal membranes, etc., and suspending these vessels in pure water. Under such conditions salts, sugar, alcohol, and ordinary solutes pass readily through the parchment, but suspensoids do not pass through at all. This offers a ready means of freeing suspensoids from salts, which often interfere seriously with the stability of the suspensions. Other sols are more stable in the presence of electrolytes, and may sometimes be precipitated by dialysis. It was, in fact, the difference in diffusing power which first led to a distinction between "crystalloids," which readily diffuse through membranes, and "colloids," which do not. This statement applies both to sols and to gels.

Dialysis is a slow process, requiring many days when a sol is to be freed from dissolved substances completely. It cannot, in general, be accelerated by immersing a sol in hot water, since this is likely to precipitate the sol. As dialysis depends upon diffusion of a dissolved substance through a membrane into a region where its concentration is lower, the rate of dialysis depends upon the area of membrane used and the difference in concentration between the inside and outside liquid. Hence a vessel composed entirely of membrane is used to enclose the sol, and a stream of distilled water is sometimes passed into the outer vessel at a sufficient rate. Toward the end of such a dialyzing process the

difference in concentration of diffusing substance becomes very small, and the rate very slow.

Methods of Preparing Sols.—Reduction of a solution of gold chloride has already been mentioned; similar reduction of other salt solutions by suitable reagents has been employed for sols of silver, platinum, and related elements. Sols readily result when the vapor of a metal formed in an electric arc is suddenly chilled by immersing the arc in water. Sols of gold, silver, copper, platinum, carbon, etc. are prepared in this way. When electrodes of oxidizable metals are used, a sol results which is probably an oxide or hydroxide of the metal; this is the case with iron, zinc, and aluminum; but these metals give a pure metal sol in non-oxidizing liquids such as hydrocarbons. In the latter case some carbon sol is probably formed at the same time as a result of reduction of the organic substance at the cathode.

Ferric hydroxide sol is formed on boiling a dilute solution of ferric chloride or acetate. This sol should be dialyzed to free it from salts if it is to be kept for a long time. Silver iodide, dissolved in strong potassium iodide solution, forms a suspensoid when the solution is poured into a large quantity of water. Sulfur dissolved in alcohol precipitates as a fine suspensoid when a large quantity of water is added. Sols of insoluble sulfides (As_2S_3, CdS, etc.) may be prepared by direct precipitation, which is sometimes followed by dialysis to remove the salt or acid formed.

Certain substances which dissolve in water as true solutes so act upon precipitates as to convert them into suspensoids, the most common case of inorganic sols being that in which the salt has an ion in common with the precipitate. Thus silver halides are converted into sols by dilute silver nitrate or the corresponding potassium halide; sulfides, such as cadmium sulfide, zinc sulfide, mercuric sulfide, and lead sulfide, are rendered colloidal by hydrogen sulfide; metallic oxides by strong alkali hydroxides. In some cases this action is reversible, as in that of metallic sulfides which can be made into suspensoids by hydrogen sulfide, thrown down by boiling it out, taken up again by passing hydrogen sulfide into a suspension of the precipitate, and this process may be repeated over and over again.[1]

[1] See Bancroft, *Brit. Assoc. Adv. Sci., Rept.*, 1918, 5; Draper, *Chem. Ind.*, **44**, 500T (1925).

Determination of Molecular Weights.—Sols do not appreciably lower the vapor pressure or freezing point of the solvents in which they are dispersed; their osmotic pressures are either zero or very small, and hence their molecular weights are very high. It is uncertain whether osmotic-pressure measurements carried out on these substances really represent the osmotic pressure of the colloidal substance itself, and not some contaminating solute, in spite of great care used in purifying the sols. Molecular weights so determined are often many thousands, and far from concordant. Doubtless such slight osmotic pressures or freezing-point depressions as are observed are partly due to impurities. It will be clear from considerations to be given presently that colloidal particles are far larger than ordinary molecules, and that ordinary molecular weight methods are quite unsuited to studying them.

Viscosity and Density.—Densities of colloidal suspensions, calculated on the assumption that the sol is a mixture of solid particles in suspension in a liquid and without any effect upon it, agree with those based on experiment. This is not surprising in view of the small concentrations of suspended material usually encountered, as these are usually less than a tenth of 1 per cent. Sols generally have viscosities which differ but little from that of the pure suspending medium, but in some sols having a high percentage of suspended matter the viscosity increases with colloid concentration more rapidly than can be explained by allowing for the volume of colloidal material.

Rate of Settling of Suspensions.—If it be assumed that a particle is a sphere of radius a and density d, and that it is settling through a gaseous or liquid dispersing medium of density d' and viscosity η under the influence of gravity g, its rate of settling is given by Stokes' law,

$$v = \frac{2a^2(d - d')g}{9\eta}.$$

Thus the rate at which a particle settles becomes slower as the density of the particle approaches that of the suspending medium. Under the influence of a force greater than gravity (for example, in a centrifuge) the rate of settling can be correspondingly increased.

Experiments by Perrin[1] have shown that this equation describes accurately the rate of settling for dilute suspensions and that the rate may be employed to determine the radius of the particles.

The law fails when the particles are about 10^{-5} cm. or smaller in diameter, for with such particles the Brownian movement, to be explained below, is sufficient to maintain them permanently in suspension.

Particles in a concentrated suspension settle with uniform velocity more slowly as the concentration increases. A 25 volume per cent suspension of silica in water settles about one-half as fast as the rate calculated from Stokes' law.[2] Stokes' law applies also to the settling of fog or dust particles in air, provided the particles are large compared to the mean free path of the molecules of the medium.[3] In other words, the law does not apply to particles settling through air at very low pressures.

Electrical Properties.—Sols have a very small effect upon electrical conductivity, and this small effect is in all probability due to traces of electrolyte adsorbed on the particles.[4] Either on account of adsorbed ions or as a result of electric charges due to friction between a particle and its surrounding liquid, suspensoids appear to be charged. When placed in an electric field, some suspensions move toward the anode, and are therefore negatively charged. Among these may be mentioned most colloidal metals, arsenious sulfide, and silver iodide. Other colloidal suspensoids move to the cathode and are, therefore, positively charged; most hydroxide sols are in this class. The belief that adsorbed ions are responsible for charges is supported by the precipitation of positive sols by negative sols. The opposite belief is supported by experiments in which a colloidal substance is held stationary in an electric field, in which case water is caused to move past the colloid. Arsenious sulfide moves toward the anode when the water is stationary; if the sulfide is held stationary (as in a membrane), water flows toward the cathode. Thus the displacement of one substance relative to the other is the same no matter which

[1] "Die Atome" (1914).

[2] Gerke, Adams, and Glasson, not yet published.

[3] Millikan, *Phys. Rev.*, **32** (1911).

[4] Whitney and Blake, *J. Am. Chem. Soc.*, **26**, 1339 (1904).

one is made stationary. This movement in an electric field is applied industrially in purifying china clay, in tanning, in medicine, and for separating colloidal and non-colloidal mixtures.[1] The mode of action is similar to that in the Cottrell precipitator for smoke and dust, in which fine particles suspended in air are caused to precipitate on a charged netting or set of chains.

The Ultra-microscope.—This instrument does not render particles *visible* which are invisible in an ordinary high-power microscope, but it shows that such particles are present by

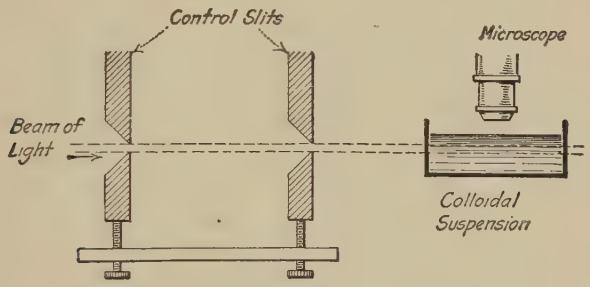


FIG. 78.—Diagram of an ultra-microscope.

a bright spot of light radiated from each particle. Nothing whatever as to the size or color or shape of a particle is learned from its effect upon the eye when viewed through an ultra-microscope; yet the apparatus is justly entitled to its name, since it shows the presence of a particle which cannot be seen at all in an ordinary microscope. A rough illustration of the principle on which it is based is afforded by the beam of light from a projection lantern in a darkened room, the so-called Tyndall effect. This shows particles of dust or smoke suspended in the air which are quite invisible when the room is thoroughly lighted, but does not show the color of the particles. A beam of light passed through clean air shows no such effect. The ultra-microscope merely magnifies highly a small portion of such an illuminated area of a suspension in a liquid medium, which is made so dilute that light radiated from each particle reaches the eye without interference from some other particle, as shown

[1] BRIGGS, *Brit. Assoc. Adv. Sci., Rept.* **1918**, 39.

in Fig. 78. Under similar conditions a concentrated suspension gives only a uniformly bright field in which no individual particles are rendered visible.

A particle 10^{-5} cm. in diameter is invisible under the highest power of microscope, but the effect of such a particle is clearly seen under an ultra-microscope. Particles far smaller in diameter than a wave length of visible light are able to show their presence by radiating light in the ultra-microscope, and the number of such particles in an illuminated volume may be counted. When the area of field under the microscope is known, and the depth of illuminated area is measured and regulated by a micrometer slit between the arc light and vessel containing a sol, a count of the spots of light in such a field gives the number of particles in a known volume. Even with very dilute sols it is often necessary to dilute them with large quantities of pure water before a count is possible. For this dilution ordinary distilled water is quite unsuited, as it contains thousands of visible particles in a drop. Specially prepared "optically empty" water is required, and its preparation involves special methods.

The size of particle detected by an ultra-microscope depends chiefly upon the intensity of illumination; the lower limit is not far from 10^{-7} cm., which is about 0.2 per cent of the wave length of visible light.

Brownian Movement.—Molecules in a liquid are in rapid though tumultuous motion of the kind outlined in connection with the kinetic theory of gases. A colloidal particle is very large compared to the diameter of a single molecule, and it is continuously bombarded on all sides by great numbers of molecules. Occasionally, the pressure due to this bombardment is for the moment greater on one side of the particle than on the other, and the particle is urged forward until a new distribution of impacts hurls it in another direction. The excursions due to these movements depend mainly on the size of the particles, and the movements correspond exactly with that predicted by the molecular theory.

Here we have reproduced in a way visible to our eyes the random unordered continuous motion of molecules postulated in connection with the kinetic theory of gases. This motion takes

place as a result of impacts with real molecules, but it makes a colloidal particle behave as it if were a single molecule. This motion was first observed by the botanist Brown on plant cells which were visible in an ordinary microscope; the movement was little more than an irregular oscillation, whose real cause remained long unsuspected. From equations based upon the kinetic theory it may be shown that the amplitude of this vibration is directly related to the diameter of the particle and the viscous resistance of the suspending medium. Thus what is a slow-oscillation effect produced upon a plant cell or small bacillus in an ordinary high-power microscope becomes, for a much smaller colloidal particle, a lively zigzag motion, as shown by the cone of light radiated from it in an ultra-microscope.

A reliable method of determining the size of suspended particles is based upon their Brownian movement, the equation for which is used in another way in the next paragraph. In this equation the radius of a particle may be determined if we assume a value for Avogadro's number of molecules in a gram-molecular weight of gas; or from counting particles and an analysis of the sol we may determine the radius, perform the reverse calculation, and compute a value of Avogadro's number. The latter procedure is more interesting.

Brownian Movement and Avogadro's Number.—A relation may be derived between the intensity of Brownian movement, the radius of the particle, the viscosity of the dispersing fluid, and the number of molecules of gas in a gram-molecular weight. Since colloidal particles are bombarded by molecules in a wholly random way, they will have the random motions of a large gas particle, and will behave as such. Upon this assumption, the equation, in terms of the mean displacement d in a unit of time t, is

$$\frac{d^2}{t} = \frac{RT}{3N\pi r\eta},$$

where r is the radius of a particle and N is Avogadro's number, η being the viscosity of the liquid suspending medium. Experiments based upon observation of displacements in small time intervals lead to values of Avogadro's number between 6.2×10^{23} and 6.9×10^{23}, in good agreement with other methods.

Distribution of Particles under the Influence of Gravity.—A suspension of heavy particles tends to separate out the solid under the influence of gravitational attraction, and is partially prevented from so doing by Brownian movement, in much the same way that molecules of the atmosphere are attracted to the earth by gravity and prevented from settling upon it by the intensity of their molecular motion. The equation expressing the variation in density of the atmosphere with the altitude contains N, the number of molecules in a gram-molecular weight. A colloidal suspension of particles of uniform size which has reached settling equilibrium distributes itself in the same way that the atmosphere is distributed under the action of gravity, thus reproducing within reasonable space the effect for which the atmosphere requires several miles of altitude. From determinations of the number of particles per cubic centimeter at equilibrium, the variation of density with altitude may be established, and used to calculate a value of Avogadro's number N. If n_1 is the number of particles per unit volume at a level which we may call zero height, and n_2 is the number at another level h cm. above the first one, the equation for change of concentration with h is[1]

$$2.303 \log \frac{n_1}{n_2} = \frac{Nmgh}{RT},$$

[1] The derivation is based upon the assumption that the colloid particles exhibit the same behavior as molecules of an ideal gas. Let ρ be the density of colloidal particles in the mixture; then ρdh is the mass of an element of thickness. The change of pressure with h is then

$$dp = -\rho dh.$$

For ρ substitute Nm/v, where N is Avogadro's number, v is the molecular volume, and m is the apparent mass of a particle, that is, the difference between its mass and that of the solvent it displaces. It should be noted that Nm is the molecular weight. If, now, we divide the above equation by $pv = RT$, we have

$$\frac{dp}{p} = \frac{-Nmg}{RT} dh.$$

On integrating between limits and noting that the ratio of pressures is equal to the ratios of the number of particles per cubic centimeter, we have

$$2.3 \log \frac{n_1}{n_2} = \frac{Nmg}{RT} (h_2 - h_1),$$

where $(h_2 - h_1)$ is the h of the equation in the above text.

where m is the difference in mass between a colloidal particle and the volume of solvent it displaces, g is the acceleration of gravity, and N is Avogadro's number. Investigations based upon this equation[1] lead to a value for N of 6.8×10^{23}.

Precipitation of Colloids.—As has been mentioned before, most suspensoids are electrically charged, probably as a result of adsorbed ions on the surface of the suspensoid particles. Ionic adsorption is a selective process, some ions being more strongly adsorbed than others. When to a positively charged sol a solution is added containing readily adsorbed negative ions at low concentration, these are adsorbed and neutralize the electric charge of the particles so that they no longer repel each other. Coagulation or precipitation takes place, and it has long been recognized that this ionic adsorption is highly specific, both in regard to the colloid and the ions. A general rule, to which there are occasional exceptions, is that ions of higher valence are more strongly adsorbed (and therefore more effective in producing precipitation) than ions of lower valence. Thus for most negatively charged suspensoids, ferric salts, aluminum salts, and trivalent cations in general, are most effective as precipitants, that is, produce coagulation when added in the smallest concentrations; lead and barium salts next, then heavy monovalent ions, such as silver, and finally the alkali ions are least effective. Similarly, positively charged sols are more readily precipitated by sulfates than by monovalent anions at equivalent concentrations. Among the latter the order of decreasing precipitating effect[2] is sulfocyanate, iodide, chlorate, nitrate, chloride, acetate, phosphate, sulfate for albumin and certain other colloid; but the precipitating power of these ions is in the reverse order for some colloids.

Precipitation also takes place when a positively charged sol is added in proper quantity to a negatively charged sol, each neutralizing the charge carried by the other. It does not follow that a chemical compound is formed, though the coagulated material may seem to be a compound. For example, ferric hydroxide sol precipitates arsenious sulfide sol, but probably

[1] PERRIN, "The Atom" (1913), a very readable book. See also DUSHMAN, *Gen. Elec. Rev.*, **18**, 1159 (1915).

[2] BANCROFT, *J. Phys. Chem.*, **19**, 352 (1915).

does not form ferric thioarsenite. It seems probable that precipitation is due to a reaction of the adsorbed stabilizing electrolyte in many cases. In general, suspensoids are much more sensitive to electrolytes at very small concentrations than are emulsoids.

Protective Colloids.—Certain substances have a conspicuous property of stabilizing colloidal suspensions. Thus a dispersoid of silver chloride is maintained in a stable state by gelatin in a photographic film, and the success of a film is largely dependent upon its retaining a uniform dispersion of this silver chloride. Gelatin and other protein substances are, in fact, the most common protective agents, though gum arabic, dextrin, starch, casein, and soap are also effective to a greater or less extent, and tannic acid is used to protect the graphite suspensions used as lubricants. The action of electrolytes in rendering insoluble substances colloidal, mentioned in a previous paragraph, is not thought to be a protective colloidal action, but more probably an adsorption effect of a common ion. There is no reason to doubt that adsorption is also active in the mechanism of protective colloids, though a simple and quite plausible explanation is that the protective substance coats the suspended particles with a very thin layer of protecting colloid. Substances which are effective in this respect are themselves able to form very stable gels.

Soap Solutions.—The extensive researches of McBain and his associates[1] have brought to light another colloidal condition which seems to be characteristic of soaps in aqueous solution. These solutions conduct electricity to about the same extent as other salts at the same equivalent concentration, but they produce a depression of the vapor pressure of solvent which would be expected of a non-ionized solute. His studies have shown that soaps are not hydrolyzed to the large extent formerly assumed, but that a colloidal aggregate of the negative ions forms which he calls an "ionic micelle." If we take sodium palmitate as an example, and let P^- denote the palmitate ion,

[1] McBain and others, *J. Chem. Soc.* (London), **101, 105, 113, 115, 117, 119, 121.** See especially pp. 1–31 of the "Report on Colloid Chemistry," *Brit. Assoc. Adv. Sci.* (1920) and pp. 244–263 of the 1922 report.

an important part of the effect produced when soap dissolves in water may be represented by the equation

$$xNaP = xNa^{+} + P_x^{x-}.$$

The chief difference between this condition and that of an ordinary ionized solute is the aggregation of negative ions into a large (colloidal) group possessing about the same *equivalent* conductance as a negative ion. There are also present in a soap solution simple sodium palmitate molecules, colloidal soap $(NaP)_y$, and simple palmitate ions. The proportion of these various solutes present in solution varies greatly with the concentration. In dilute solutions NaP and P^- predominate, and in a normal solution 50 per cent exists as $(NaP)_y$ at 90° and about 30 per cent as the ionic micelle. Aqueous solutions of soaps when functioning as detergents are seldom at concentrations greater than 0.01 molal or less, so that neither the colloidal soap nor the ionic micelle contribute very largely to the useful properties commonly associated with soap. Probably the effect of simple sodium palmitate molecules upon the surface tension is chiefly responsible for the cleansing action of soap. This is discussed more fully in a later paragraph.

Donnan Equilibrium.[1]—We may consider here the *equilibrium* which prevails on the two sides of a dialyzing membrane which is permeable to ordinary ions but not to a colloid or its ion. If congo red is taken as an illustration, we may write its formula NaR to indicate that it is a sodium salt of a radical of colloidal character. We shall assume that a solution containing this salt and sodium chloride is separated from pure water by a membrane permeable to sodium chloride and its ions, but not to NaR or to the colloidal ion R^-, which is formed when congo red ionizes. It may be that this ion forms a micelle $(R^-)_x$, as in the case of soaps. Dialysis will proceed, and *at equilibrium* some of the sodium chloride and all of the congo red and its negative ion will be on the original side of the membrane, and sodium chloride alone will have diffused through the membrane. The equilibrium

[1] *Z. Electrochem.*, **17**, 572 (1911). For a more detailed discussion of this equilibrium and its bearing on colloid chemistry, see Loeb, "Proteins and the Theory of Colloid Behavior," McGraw-Hill Book Co. Inc. (1922) and Bogue, "Colloidal Behavior," McGraw-Hill Book Co., Inc. (1924).

condition may be shown as follows, if the dotted line represents the membrane.

Na^+R^-	Na^+Cl^-
Na^+Cl^-	
(1)	(2).

Since a positive ion may not diffuse through the membrane without a negative ion except by overcoming very large electrostatic forces, the ions of sodium chloride must diffuse through together. The number of ions which strike the membrane per unit of time is proportional to their concentration. If $(Na^+)_1$ and $(Cl^-)_1$ represent the concentrations of sodium ions and chloride ions on the left-hand side at equilibrium, the rate of diffusion through the membrane into the right-hand side is proportional to the product of these concentrations, $(Na^+)_1(Cl^-)_1$. But since equilibrium prevails, diffusion in the reverse direction takes place at the same rate and this rate must be proportional to the product of the concentrations on the right and the same proportionality constant. That is, at equilibrium

$$(Na^+)_1(Cl^-)_1 = (Na^+)_2(Cl^-)_2.$$

The concentrations $(Na^+)_2$ and $(Cl^-)_2$ are necessarily equal, since only sodium chloride has diffused through the membrane, but $(Na^+)_1 = (Cl^-)_1 + (R^-)$. Thus the concentration of sodium chloride on the side of the membrane where it alone is present is greater than its concentration on the side with the colloid, but the *total solute* concentration is greater on the side containing the colloid.

This equilibrium may be applied to the swelling of gelatin immersed in an acid solution, for the proteins are amino acids which combine with hydrogen ions (above a certain concentration) to form salts. If P denotes the protein molecule, $P + H^+Cl^- = PH^+Cl^-$. When the gelatin has swelled to equilibrium the product $(H^+)(Cl^-)$ in the solution within the gelatin must be the same as in the external phase. Denoting the concentration in the presence of the colloid by the subscript 1, in the inside solution we should have

$$(Cl^-)_1 = (H^+)_1 + (PH^+),$$

whence at equilibrium

$$(H^+)_1(Cl^-)_1 = (H^+)_2(Cl^-)_2$$

or,

$$[(H^+)_1 + (PH^+)]\ (H^+)_1 = (H^+)_2{}^2.$$

It has been shown by Loeb[1] that, when the hydrogen ion concentration is greater than 2×10^{-5} (*i.e.*, pH = 4.7, to use the original notation), gelatin combines with hydrogen ions and forms gelatin chloride; at a lower hydrogen ion concentration metal proteinates form, and at this hydrogen ion concentration it combines with neither hydrogen ions nor hydroxide ions. This is called the iso-electric point for gelatin. Thus, whether the gelatin combines to form a complex positive ion or a complex negative ion, the *total solute* concentration within it is greater than in the outer solution with which it is in equilibrium. In other words, the activity of water, as measured by its vapor pressure, is less within the gelatin, and water tends to pass into the gelatin. This is probably the explanation of the swelling of gelatin in water.

Emulsoids.—These differ from suspensoids in that both phases are probably liquid, and the ratio of dispersed phase to dispersing medium is much larger. In the sols already considered the dispersed phase was seldom present in greater quantity than a fraction of 1 per cent; emulsoids have been prepared in which the dispersed phase was 99 per cent of the whole, only about 1 per cent being the continuous or dispersing phase. Emulsions of oil in water (when the disperse phase amounts to one part per thousand) and similar dilute emulsions are properly considered as suspensoids, and are not included in this discussion.

Emulsions containing large percentages of disperse phase are stable only when the interfacial tension between the phases is low,[2] and this lowering of surface tension is sometimes brought about by dissolving soap or other substance in the dispersing medium.

Concentration in Surfaces.—It is a general law that substances which lower the surface tension of a solution accumulate in the surface, producing there a higher concentration of solute than is

[1] Reference quoted above.

[2] HATSCHEK, *Rept. Brit. Assoc. Adv. Sci.*, **1918**, 17.

present in the bulk of liquid. Any substance which will lower the surface tension may act as an emulsifying agent. The relation between u, the excess of solute per unit of surface or interface, c, the concentration, and the rate at which surface tension changes with concentration, $d\gamma/dc$, is

$$u = -\frac{c}{RT}\frac{d\gamma}{dc},$$

which is called the Gibbs' adsorption equation. From this equation it will be seen that if $d\gamma/dc$ is positive, surface tension is increased by the solute, u is negative, and there is no accumulation of solute in the surface, but a deficiency of it. When the solute lowers the surface tension, $d\gamma/dc$ is negative and u is positive; that is, solute accumulates in the surface in excess. If a froth is formed on such a liquid in which the surface tension has been lowered, excess solute will be found in the froth.

In moderately strong solutions of substances which depress the surface tension, the surface itself consists of a layer of the dissolved substance *one molecule deep*,[1] and there is no transition layer in which the concentration varies progressively at points further from the surface into the solution. The amount of solute required to form this layer may be calculated from the Gibbs equation, and from this quantity of solute in the surface layer may be calculated the diameter and cross-section of the molecules forming the layer. The data so found are in agreement with those obtained from other methods of measuring molecular diameters. For example, Langmuir found that the molecular cross-section in the surface was 24×10^{-16} sq. cm. per molecule for palmitic acid. On page 95, 21×10^{-16} was found from the spreading of a film of palmitic acid on the surface of water. Recent measurements of the surface tension of soap solutions against a benzene interface[2] have given 40 to 47×10^{-16} for the molecular cross-section of sodium oleate adsorbed into the interface. With solutions of inorganic salts, where the surface tension is greater than that of water and increases linearly with the concentration, there is a deficiency of solute in the surface layer proportional to the concentration. This surface layer, therefore, consists of water molecules in excess.

[1] Langmuir, *Proc. Nat. Acad. Sci.*, **3**, 251 (1917).

[2] Harkins and Zollman, *J. Am. Chem. Soc.*, **48**, 58 (1926).

Surface Tension and Emulsion Formation.—It has long been known[1] that a decrease of surface tension is produced by those substances which aid emulsification, and that, therefore, a lowering of surface tension is essential to the formation of stable emulsions. The first sodium salt of the series of fatty acids to produce appreciable lowering of surface tension when it is added to water is sodium laurate, and this is the first salt in such a series to aid appreciably in forming emulsions of oil in water. It is the first salt of the series to form a soap with marked froth formation, and having cleansing properties. There is at least a rough proportionality between surface-tension decrease and emulsifying power so far as emulsions of oil in water are concerned.

When sodium oleate is dissolved in water, a very rapid decrease in surface tension takes place at the interface between solution and vapor with increasing concentration of the soap, until at 0.002 normal the surface tension reaches its minimum value[2] of about 25 dynes per centimeter. Further additions of sodium oleate produce no significant change, from which it may be concluded that the *surface is saturated.* In other words, the interface contains all the soap it is capable of holding when the bulk of the solution is very far from saturated. The arrangement is entirely similar to that assumed by oleic acid films spreading upon water (page 93); a monomolecular layer of soap exists at the interface, which is saturated with sodium oleate at any concentration over 0.002 normal. Water and oil when shaken together do not form a stable emulsion, *i.e.*, the layers soon separate after shaking is discontinued. If a little sodium oleate is dissolved in the water layer, and this is then shaken with oil, a stable emulsion forms in which droplets of oil are suspended in a continuous phase of dilute aqueous soap solution.

If a solution of sodium oleate is 0.005 molal the interfacial tension between benzene and the solution is about 5 dynes per centimeter; the interfacial tension between benzene and pure water is 35 dynes. Since the oleic group is highly soluble in benzol and the sodium or NaCOO— group is not, the molecules of soap in the interface probably arrange themselves with the

[1] Donnan and Potts, *Kolloide-Z.*, **9**, 159 (1911).

[2] Harkins, Davies, and Clark, *J. Am. Chem. Soc.*, **39**, 541 (1917).

latter group toward the aqueous phase and the oleic groups toward the benzene phase. Inversion of the emulsion takes place, and benzene becomes the continuous phase in which droplets of water are suspended when magnesium oleate (which is insoluble as a whole in water) is substituted for sodium oleate as the emulsifying agent.

In either case the stability of the emulsion depends upon the formation in the interface of a film of low interfacial tension. Since the energy required to form the large area of interfacial surface in a fine emulsion is liberated (as free energy) when the emulsion separates into two continuous phases, there would be a smaller liberation of energy, and thus a smaller tendency toward separation, for low interfacial tensions.

Structure of Emulsions or Gels.—Some authorities state that viscous emulsions and gels probably have the same structure. A stiff jelly is often convertible into an emulsion by heating, and it returns again to the state of jelly after cooling. In each case microscopic droplets of one liquid phase are completely surrounded by a continuous film of the other liquid phase. It is not necessary that the continuous phase be present in greater quantity than the dispersed phase; a cross-section of an emulsion in which the disperse phase is present in excess might look something like a section through a comb of honey, with thin films of continuous phase (represented by the wax cell walls) surrounding droplets of dispersed phase. It is only necessary that there be enough dispersing phase to form a *continuous* film between each droplet and the next neighbors to it. Gelatin gel is considered as a dilute solution of gelatin dispersed in a more concentrated one, the stiffness of such a jelly being due to resistance to shearing of the stronger solution. That this is not incompatible with the properties of liquids in general is shown[1] by the fact that stiff non-flowing gels have been prepared in which 99 per cent of mineral oil is dispersed in 1 per cent of a soap solution. The oil is the disperse phase, not the soap solution, as may be shown by adding a drop of oil to such a gel. If oil were the dispersing medium (continuous phase), it should spread through the whole gel, but it remains as a single drop in with the smaller droplets.

[1] PICKERING, *J. Chem. Soc.* (London), **92**, 2001 (1907).

There are sharp differences of opinion as to the structure of gels, however. Some believe them to be a single phase. Weiser[1] states that the vast majority of investigators believe jellies to be two-phase systems in which a cellular or network arrangement of solid phase is permeated by a liquid phase. At the present time it does not seem possible to decide definitely among these various views; perhaps all of them are correct for certain gels, and no one is of general application to all of the inorganic and organic systems collectively called gels.

Gels in the Ultra-microscope.—Gelatin and other gels show under the ultra-microscope a slight Tyndall effect which increases with concentration, but these gels do not show individual particles as in the case of sols. Such light as is seen in an ultramicroscope is probably due to a difference in index of refraction of the liquid phases forming a gel. There is no Brownian movement of the droplets of disperse phase. In very dilute dispersions of oil in water Brownian movement is observed, but these are not properly considered gels, since the quantity of disperse phase is very small, and these emulsions have the property of suspensoids to a far greater extent than they resemble gels.

Viscosity of Emulsoids.—Emulsoids have viscosities which, even for very dilute gels, are much higher than that of the "solvent," and which seem to depend upon the rate of shear within the fluid dispersing medium. No satisfactory theory relating to the viscosity of colloids has been developed, but it is known that very slight changes in a gel produce a marked effect upon its viscosity, and hence viscosity measurements are a delicate means of tracing such changes. About all that can be deduced, however, is that a change has taken place, the nature of which is matter for speculation or empirical interpretation. Use of such methods is extensive in the rubber and nitrocellulose laboratories,[2] where the age of an emulsoid is a very important factor in determining its properties. Lack of a satisfactory theory does not interfere with the use of these measurements as control methods.

[1] BOGUE, "Colloidal Behavior," vol. I, p. 378. Chapter XV of this volume (by H. B. Weiser) discusses at length the rather inconclusive evidence in support of the various views regarding gel structure, and gives references to the voluminous literature devoted to it.

[2] HATSCHEK, *Repl. Brit. Assoc. Adv. Sci.*, **1917**, 22.

References.—Complete and thorough reviews of the whole field of colloid chemistry are given in the excellent "Reports on Colloid Chemistry" issued by the British Association for the Advancement of Science. The first of these reports was published in 1917, and later ones in 1918, 1920, 1922, and 1923. Many of the facts in this chapter have been taken from these reports. The industrial applications of colloid chemistry are there reviewed briefly, with full references to the original sources of information, of which over a thousand are given in the first report. There are, in addition, several textbooks of colloid chemistry available in English. Practical applications of colloid chemistry to lubrication, waterproofing, plasticity of clays, and colloidal fuel are reviewed in *J. Ind. Eng. Chem.*, **12**, 434 (1920); the setting of cement as influenced by its colloids is discussed in the British Association report. Reference should also be made to BANCROFT's "Applied Colloid Chemistry," McGraw-Hill Book Co., Inc. (1926) and to BOGUE's "Theory of Colloidal Behavior," McGraw-Hill Book Co., Inc. (1925).

CHAPTER XVI

ELECTROCHEMISTRY

Chemical reactions at the electrodes, the conductance of solutions of ionized solutes, and transference effects have been considered in an earlier chapter. In this chapter we shall be concerned mainly with another aspect of electrochemistry, the potentials of electric cells, and the maximum electrical energy to be derived from them. The energy of any electric process is the product of potential, current, and time. In the usual units of volts, amperes, and seconds the energy unit is 1 joule, or volt-ampere-second, 4.185 of these units being equivalent to 1 small calorie.

The changes taking place at the two electrodes of a voltaic cell from which an electric current is being derived may sometimes be reversed by causing electricity to pass through the cell in the opposite direction. Faraday's law described the relation between *quantity* of electricity and quantity of chemical change, whether the cell is producing an electric current at the expense of the chemical energy associated with the reaction, or absorbing electric energy and changing it into chemical energy while the reaction is reversed. But the *potential* or voltage of the cell depends to a marked extent upon the rate at which electricity passes through it. Experiment shows that the maximum potential to be derived from an electric cell in which a chemical reaction occurs is obtained when the current withdrawn from it is very small. Further, the minimum potential required to reverse the chemical reaction is associated with the smallest measurable current. These potentials or voltages become substantially equal for very small currents, and this electromotive force corresponds to a reversible change in the thermodynamic sense. Thus the maximum electrical work to be obtained from any chemical change results when this change is brought about in an electric cell which is made to operate against an opposing force

only infinitesimally less than its maximum voltage. This maximum voltage is measured on a potentiometer.

A potentiometer is an arrangement for comparing one electromotive force with another which is already known. Suppose a storage battery, whose electromotive force is unknown, to be connected to the ends of a uniform wire 10,000 mm. long and of high resistance. The potential drop along this wire is uniform, but unknown. In order to determine the electromotive force of the storage battery, and hence the potential drop per millimeter of wire, a "standard cell" of known electromotive force

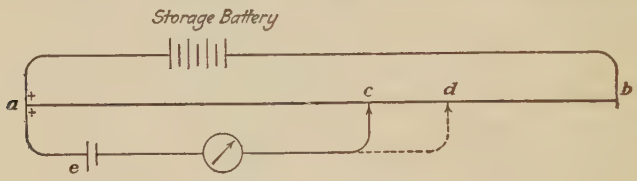


Fig. 79.—Potentiometer diagram.

is placed in position e of Fig. 79, in series with a galvanometer, and contact is made at such a point c that there is no deflection of the galvanometer. Commonly, the Weston cell, electromotive force 1.01872 volts at 25°, is used, but any other battery of known electromotive force will serve. The potential of the storage battery bears the same relation to that of the standard cell as ab does to ac, for since there was no deflection of the galvanometer when contact was made at c, there was no current flowing under these conditions, and therefore the electromotive force of the standard cell was opposed by an exactly equal one supplied by the storage battery. The wire ab being of uniform resistance, only the part ac/ab of the total potential from the storage battery was required to be equal to that of the standard.

If we now replace the standard cell by one of unknown electromotive force and find such a point of contact d that there is no current flowing through the galvanometer, then the new cell has an electromotive force which is to that of the standard as ad is to ac.

Hydrogen-chlorine Cell.—A chemical reaction involving ions may serve as a source of electric energy if the reaction can be made to take place at two different parts of a system through a

transfer of electric charges from one place to another. For example, the union of hydrogen and chlorine to form hydrochloric acid may be made to serve as a source of electric energy. Hydrogen molecules are not electrified, nor are chlorine molecules; in a solution of hydrogen chloride, the main constituents are hydrogen ions and chloride ions. The chemical reaction $H_2 + Cl_2 = 2HCl$ (in solution) may be made to take place at two electrodes. If we denote a faraday of positive electricity by the sign $\oplus$, the reaction

$$H_2 + 2\oplus = 2H^+$$

occurs at one electrode, the "hydrogen electrode," and the reaction

$$Cl_2 = 2Cl^- + 2\oplus$$

takes place at the other electrode. These two reactions occur at the same time, of course, and the transfer of ions from one electrode to the other constitutes the electric current through the solution. In the first reaction, oxidation, *i.e.*, increase in positive charge or positive valence, takes place, and this electrode is therefore the anode. We shall retain our definition of an anode which was previously given, namely, the anode is the electrode at which *oxidation* occurs. The *reduction* of chlorine gas to chloride ions takes place at the cathode.

A hydrogen electrode consists of a plate of platinized platinum dipping into an acid solution, and in contact with hydrogen gas. A slow current of gas is bubbled over the plate in order to stir the acid around it and keep the electrode thoroughly saturated with hydrogen gas. A chlorine electrode is prepared in the same way, and the two electrodes are dipped into hydrochloric acid. The electromotive force so set up is measured with a potentiometer as explained above. A diagram of the apparatus is shown in Fig. 80. Electrochemical reactions take place at each electrode which are strictly in accordance with Faraday's law, 2 faradays ($2 \times 96{,}500$ coulombs) being produced when one mol of hydrogen and one of chlorine unite to form two mols of hydrogen chloride in solution.

It is well known that when hydrogen and chlorine are mixed, they combine spontaneously, and with the evolution of much

energy. Since the operation of the cell which we have been discussing results in the formation of hydrogen chloride in the solution, this is also a spontaneous process capable of performing work. If E is the maximum electromotive force of this cell, as measured on a potentiometer, and F denotes 96,500 coulombs of electricity, the maximum electrical work obtainable from this chemical reaction is $2EF$.

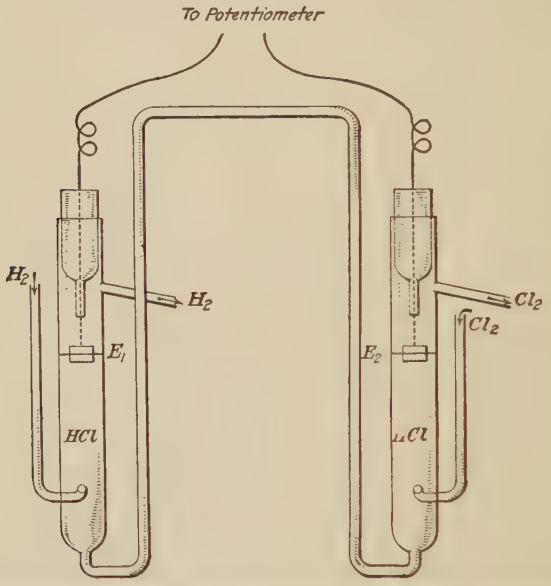


FIG. 80.—Diagram of a cell for deriving electric energy from the union of hydrogen and chlorine.

The electrical work, $2EF$ joules, will not be equal to the heat of the chemical reaction occurring in the cell, for this could be true only in case no heat was absorbed by the cell during its operation, and cells usually absorb or evolve some heat while they produce electricity from chemical reactions. As we have seen in the study of thermochemistry, the *total* energy change associated with a change in state depends only on the change which takes place. By carrying out the reaction in a calorimeter the total energy can be obtained, but this cannot be equal to the electrical energy if energy in any other form is absorbed or evolved during the operation of the cell.

It is necessary to specify more particularly than has been done so far the exact nature of the chemical process which takes place in an electric cell, or the potential E will have no definite meaning; for the electromotive force of a cell is to be used later as a measure of the spontaneity of a process, or as we shall then say, of the *free energy* available from a process. And the spontaneity of a change from an initial state a to a final state b will be less than that of a change from a to some other condition c if the system will go from b to c of itself. The change in state is completely determined when all of the factors which govern the condition of the systems before and after the change are quantitatively specified.

Thus in the above example we should write

$$H_2(1 \text{ atm.}) + Cl_2(1 \text{ atm.}) = 2H^+Cl^-(\text{in } 0.1\ m.)$$

and we should specify the temperature, say 25°. Usually it is unnecessary to specify the state of aggregation, for this is obvious from the temperature and pressure, but in special cases we may designate this by g, l, or s. In order to specify completely the state of a system we should state (a) the chemical substances of which it consists, (b) the quantity of each one present, (c) the concentrations of solutions involved, (d) the temperature and pressure, and, when necessary, (e) the state of aggregation.

Formulation of Cells.—In this chapter we shall consider only reversible cells; that is, cells in which, by passing an electric current in the reverse direction, the chemical effects attending their operation may be reversed. We shall consider as the electromotive force of a cell its maximum electromotive force as determined by a potentiometer; that is, we shall consider a cell as operating so slowly that each electrode is at all times in equilibrium with the solution around it. Solutions are considered to be present in large quantity, so that no appreciable change in concentration takes place as a result of operating the cell. This is accomplished in laboratory practice by passing only a very small quantity of electricity, but it is convenient in discussing cells to imagine a very large cell, and pass through it 1 or 2 faradays of electricity corresponding to the production of a mol of dissolved substance. When only a very small quantity of electricity is passed through a cell in laboratory practice, it is clear

that great purity of chemicals is required, otherwise the potential measured may be caused by a minute quantity of an unsuspected impurity sufficient to give an electrode reaction quite different from that which the cell is supposed to give. Cells are, therefore, set up in duplicate or triplicate and checked against one another frequently, to avoid this possible error.

The various parts of cells are separated by commas, which indicate points at which there is a difference of potential developed. This will be explained in detail presently. Denoting by M an inert metal,[1] the cell discussed above would be written

$$M + H_2(1 \text{ atm.}), HCl(0.1\ m.), M + Cl_2(1 \text{ atm.})$$

and the chemical reaction corresponding to 2 faradays of electricity is

$$H_2(1 \text{ atm.}) + Cl_2(1 \text{ atm. }) = 2HCl(\text{in } 0.1\ m.)$$

Sign of Electromotive Force.—We shall pass positive electricity from left to right through a cell as written, and in all operations of cells consider that positive electricity so passes, regardless of the actual tendency of the cell. When a cell operates *of itself* in such a way that the positive current does pass through it from left to right, its electromotive force is called positive; or when an outside potential is required in order to force positive electricity through it from left to right, its electromotive force will be called negative.[2] Thus when we write

$$H_2(1 \text{ atm.}), HCl(0.1\ m.), Cl_2(1 \text{ atm.}); E = +1.4881v.,$$

[1] The presence of an inert metal at any gas electrode is always understood, though in formulating cells it is not always written down. For example, Cl_2, Cl^- means that an inert metal is dipping into a solution where chloride ions are present, and is in contact with chlorine gas at the specified pressure. It would, of course, be impossible for a gas alone to function as an electrode, for metallic conduction to and from it is necessary.

[2] This is the convention adopted by Lewis, *J. Am. Chem. Soc.*, **35**, 1 (1913), and commonly used in American publications. European electrochemists employ the opposite convention. The usage here followed is in accord with that in the papers to which reference is made in this chapter. Students who prefer to write electrode reactions in terms of negative electrons may avoid confusion in sign by considering the negative current to pass from *right to left* through the cells, as do Lewis and Randall in their "Thermodynamics."

this indicates the tendency of positive electricity to pass of itself through the cell from left to right. Then at the left-hand electrode the anode reaction corresponding to 2 faradays is

$$H_2 + 2\oplus = 2H^+$$

The cathode reaction on the right is

$$Cl_2 = 2Cl^- + 2\oplus$$

and the sum of these reactions is the formation of hydrochloric acid into a solution. Since hydrogen chloride will form from hydrogen and chlorine, and since the gas so formed will dissolve in water, both of these electrode processes are able to occur without the aid of outside energy. A positive electromotive force indicates that the cell will supply electricity during its operation, at the expense of the chemical energy liberated by the reaction taking place in the cell.

It should be noted that by writing the cell in the opposite order and passing positive electricity through it from left to right, chemical reactions occur which are the opposite of those just given, and hydrogen chloride is decomposed into its elements. This is not a spontaneous process; it requires the use of outside energy. In the formulation of this cell, the facts just given are indicated as follows:

$$Cl_2(1 \text{ atm.}), HCl(0.1\ m.), H_2(1 \text{ atm.}); E = -1.4881\ v.$$

This is equivalent to saying that an outside electromotive force of at least 1.4881 volts is required to pass positive electricity from left to right through this cell.

Maximum Work and Free Energy.[1]—The ideal reversible process is one which produces such an amount of work that if this work is again expended in driving back the process (also reversibly), the initial condition of all systems involved can be completely restored. No actual process is ever reversible; but by eliminating friction, electrical resistance, and other factors involving inefficiency, it is often possible to approach the ideal reversible process to any desired degree of approximation.

[1] The terms defined below are those given by LEWIS, *J. Am. Chem. Soc.*, **35**, 1 (1913). This section and the following one are quoted, with only minor changes, from pp. 13 and 14 of his article.

The maximum work which can be obtained in passing isothermally and reversibly from a state I into a state II is of great importance because it is independent of the particular reversible process employed. If this were not the case, then by proceeding from I to II by one reversible process and returning from II to I by another reversible process, requiring less work, a certain net amount of work would be gained, and this could come only from the heat of the surroundings. And the second law of thermodynamics asserts the impossibility of producing work in an isothermal reversible cycle of changes at the expense of heat withdrawn from the surroundings.

When a system is in equilibrium with respect to certain possible changes, such changes may be made to occur in either direction by infinitesimal changes in the variables, such as temperature, pressure, etc., which determine the state of the system. By changing back to the original conditions the system will return to its initial state. Therefore any infinitesimal change occurring in a system which is in equilibrium is reversible. Thus, in any physico-chemical change, by keeping the system as near as is desired to the equilibrium conditions, it is possible to approach the ideal reversible process. The work obtainable from any change in state occurring when the system is kept under conditions of equilibrium is, therefore, the maximum work.

Since this maximum work is independent of the path by which the system passes from the state I to the state II, we may regard it as the difference between two quantities, one of which, A_1, is completely determined by the initial system, and the other, A_2, is determined by the final system. That is, we may write,

$$\text{maximum work} = A_1 - A_2 = -(A_2 - A_1) = -\Delta A. \quad (1)$$

and $-\Delta A$ may be called the decrease in the work content of the system.

Another quantity of equal importance is derived from ΔA in a way similar to that in which ΔH is derived from ΔE (page 221). Before giving a mathematical expression for this quantity, its significance may be illustrated by a concrete example. Suppose that the cell described in the preceding section operates reversibly under atmospheric pressure, giving the electrical work W_e. This quantity of work W_e represents, in fact, the work which

can be utilized for any external purpose, for example, by the operation of an electrical motor. It is not true, however, that W_e is equal to the quantity we have defined as $-\Delta A$, for, in addition to the electrical work, a certain amount of work has been done upon the cell by the atmosphere, owing to the decreased volume of the products of the reaction. If $-\Delta v$ represents the decrease in volume, it is evident that

$$W_e = -\Delta A - p\Delta v. \tag{2}$$

This important quantity, which, in general, represents the work actually available for any desired purpose, is itself dependent only upon the initial and final states of the system, and is called the free energy decrease. We shall write

$$\mathbf{F} = A + pv \tag{3}$$

and

$$\Delta\mathbf{F} = \Delta A + \Delta pv. \tag{4}$$

The quantity **F** will be called the free energy, and $\Delta\mathbf{F}$ will be called the increase in free energy accompanying the reaction in question. Since the electrical work W_e is ENF, equation (2) may be written

$$-\Delta A = ENF + p\Delta v, \tag{5}$$

whence from equation (4)

$$\Delta\mathbf{F} = -ENF. \tag{6}$$

It will be recalled that the increase in heat content, ΔH, accompanying a chemical reaction was the negative of the heat evolved by it. Similarly, the increase in free energy is the negative of the available work derived from it, other than that due to changes of p or v. When heat is absorbed by a system, its heat content increases. When work (electrical work, for example) is done upon a system, its free energy content increases, and it is capable of performing this work again when it is desired.

The Change of Free Energy with Pressure.—Let us consider the change in free energy in the simple process, of which the net result is the disappearance of n mols of a pure substance at pressure p_1, and the appearance of n mols of the same substance at pressure p_2. This may be done reversibly by allowing the

substance to expand or contract under an external pressure which is always kept equal to the pressure of the substance. Then

$$\Delta A = -\int p dv$$

and, from equation (4),

$$\Delta \mathbf{F} = -\int p dv + \int d(pv) = \int v dp. \tag{7}$$

When the substance is a perfect gas, its molal volume is given by the equation $v = nRT/p$, and the integration gives

$$\Delta \mathbf{F} = nRT \ln \frac{p_2}{p_1}. \tag{8}$$

Free Energy and Activity.—If a solute is an ideal gas, its activity in solution is proportional to its pressure above the solution, and the free-energy change attending the transfer of n mols of it from a solution in which its activity is a_1 to another in which its activity is a_2 is

$$\Delta \mathbf{F} = nRT \ln \frac{a_2}{a_1}. \tag{9}$$

This equation may also be derived for non-volatile solutes by considering an osmotic process of transfer. We shall use it to represent the free-energy increase attending the transfer of any solute from an activity a_1 to another activity a_2, even when the solute is an ion which exerts no measurable vapor pressure.

In the cell whose electromotive force is 1.4881 volts, the free-energy decrease for the change in state

$$H_2 \text{ (1 atm.)} + Cl_2\text{(1 atm.)} = 2HCl \text{ (in 0.1 } m.\text{)}$$

corresponds to the maximum electrical work available from this reaction, and we may write

$$\Delta \mathbf{F} = -2EF.$$

It should be noted in this equation that $\Delta \mathbf{F}$ is used to describe a free-energy change and that F denotes 96,500 faradays of electricity.

Whenever a given chemical change may be brought about by passing N faradays through a cell of electromotive force E, the maximum electrical work of this process is the product of quantity of electricity and potential, or ENF. If this same chemical

change, involving the same initial and final states of the system under consideration, is brought about in two different cells, each requiring the quantity of electricity NF, then if E_1 and E_2 are the electromotive forces of these two cells, $E = E_1 + E_2$, since $ENF = E_1NF + E_2NF$ according to the law of conservation of energy. In case the quantity of electricity involved is not the same in all three cells, it should be noted that it is ENF which is equal to $E_1N_1F + E_2N_2F$, whence if 2 faradays are involved in producing a change in the first cell, and one in each of the two which produce this total change in separate steps, $E = (E_1 + E_2)/2$.

Electrode Potentials.—There is at the junction between an electrode and a solution a tendency (positive or negative) for positive electricity to pass from *electrode to solution*, which tendency depends upon the electrode material, the nature and concentration of the ion formed or destroyed in solution by the passsage of electricity, and the temperature. In the cell which we have been discussing,

$$H_2 \text{ (1 atm.)}, \text{HCl (0.1 } m.\text{)}, Cl_2\text{(1 atm.)}; E = 1.4881v.,$$

the separate tendencies at each electrode may be represented by

$$M + H_2 \text{ (1 atm.)}, \text{HCl (0.1 } m.\text{)}; E_1 = x$$

and

$$M + Cl_2 \text{ (1 atm.)}, \text{HCl (0.1 } m.\text{)}; E_2 = y.$$

It is convenient to compute each electrode potential separately, and to consider every electrode as an anode. Then in any cell a positive current will pass through the solution in one direction or the other, depending upon which electrode has the greater tendency to function as an anode. The potential of the cell as a whole will be the algebraic difference between the two anode potentials, x and y. Thus if the hydrogen electrode behaves as an anode, the reaction is

$$H_2 \text{ (1 atm.)} + 2\oplus = 2H^+ \text{ (in 0.1 } m.\text{)};$$

and if the chlorine electrode is an anode, the reaction is

$$2Cl - \text{ (in 0.1 } m.\text{)} + 2\oplus = Cl_2\text{(1 atm.)}.$$

Since in the actual cell only one electrode is an anode, the tendency for positive electricity to pass through the cell as a whole is the

difference between the potential of these two cell reactions, that is,

$$E = E_1 - E_2 = x - y,$$

and the electrode of smaller potential is forced to act as a cathode. The total electromotive force of the cell is $E = x - y = 1.4881$, which may be considered as the difference of two *electrode potentials*. One of these electrode potentials represents the tendency of positive electricity to pass into solution upon hydrogen ions, and is sometimes called the electrolytic solution tension of hydrogen; the other represents the tendency of positive electricity to pass from electrode to solution with the formation of chlorine gas from chloride ions. In general, the electromotive force of any cell containing only one solution may be computed from the difference of its two electrode potentials, each considered as an anode, as in the illustration just given.

The preparation of a table of electrode potentials is, therefore, a matter of importance. But, as mentioned above, the electrode potential depends upon the concentration of solute already in the solution, and, in the case of electrode reactions involving gaseous substances, upon the pressure of the gas. This pressure is understood to be the partial pressure of the substance involved in an electrode reaction, not the total pressure.

A table of *normal electrode potentials* or specific electrode potentials, representing the tendency of a reaction to form ions into a solution where their activity is unity, may be prepared in terms of the potential of any one electrode. It will be understood that a voltaic cell always consists of two electrodes and that its total potential depends upon the difference between the tendency of positive electricity to pass from electrode to solution at two electrodes. The electrode having the smaller anodic *tendency* is then forced to function as a cathode.

It has now become customary to assume as zero the electrode potential of hydrogen gas at a partial pressure of 1 atmosphere and in contact with a metal electrode dipping into an acid solution containing hydrogen ions at unit activity. The potentials of all other electrodes are referred to this arbitrary zero. This convention does not mean that there is no tendency for the reaction $\frac{1}{2}H_2 + \oplus = H^+$ to occur under these conditions, but

only that the potential of chemical reactions corresponding to the other electrodes is greater or less than this potential by the values given.

This peculiar choice of a standard has a certain theoretical advantage for the preparation of a table of free energies. It is nevertheless unfortunate that the *standard* for electromotive potentials should be one which cannot be set up experimentally, for there is no common agreement among chemists as to the chemical composition of a solution containing hydrogen ions at unit activity or hypothetical unit molality. The composition of such a solution depends upon the activity coefficient chosen for hydrogen ion, and this, in turn, depends upon the extrapolation of data into the uncertain region where hydrogen ions are ideal solutes.

We shall consider each electrode reaction in terms of positive electricity passing from electrode to solution whether the actual tendency is in this direction or not, and we shall denote electrodes in which there is the opposite tendency (that of positive electricity passing from solution to electrode) by a negative electrode potential. The chlorine electrode is an example of an electrode at which the natural tendency is for positive electricity to pass from solution to electrode, but we write

$$Cl^- + \oplus = \tfrac{1}{2}Cl_2;\ E = \text{a minus quantity.}$$

In computing the effect of concentration upon electrode potential, the electrochemical reaction occurring at an electrode is always written with the symbol $\oplus$ on the left-hand side of the equation, and the actual sign of the electromotive force is then automatically cared for by the method of computing electrode potentials. In any cell the total potential is $E = E_1 - E_2$, where E_1 is the left-hand electrode or anode potential, and E_2 is the right-hand electrode potential. In computing the electromotive force of any cell, separate values of E_1 and E_2 are computed from the normal electrode potentials by the equation given below, and the total electromotive force of the cell is obtained by subtraction.

Electrode Potential and Concentration.—For the hydrogen electrode

$$H_2(1 \text{ atm.}),\ H^+ \text{ (unit activity)}$$

we may write the electrode potential as E^0_H; and the electrode potential E_H for any other concentration or pressure, corresponding to the reaction

$$H_2(p \text{ atm.}) + 2\oplus = 2H^+(\text{in } c \text{ molal}),$$

may be derived by considering the free-energy increase attending this change in state when it is brought about in three steps, one of which involves the specific electrode potential E^0_H. We may note that the free-energy increase of the direct change described by the equation is

$$\Delta \mathbf{F} = -2E_1F,$$

and that this must be equal to the sum of the free-energy increases for the several steps whose final result is the same change in state. These steps are

(*a*) $H_2(p \text{ atm.}) = H_2(1 \text{ atm.})$; $\Delta \mathbf{F}_a = a$.
(*b*) $H_2(1 \text{ atm.}) + 2\oplus = 2H^+(\text{unit activity})$; $\Delta \mathbf{F}_b = -2E^0_HF$.
(*c*) $2H^+(\text{unit activity}) = 2H^+(\text{in } c \text{ molal acid})$; $\Delta \mathbf{F}_c = c$.

For the first step the free-energy increase may be computed from equation (8),

$$\Delta \mathbf{F}_a = RT \ln \frac{1}{p}.$$

If it were permissible to assume that hydrogen ion is an ideal solute, we might in the third step transfer 2 mols of it from unit activity to an activity c in a solution in which its molality was also c by an osmotic process entirely similar to that just used for hydrogen gas. However, when the molality of the acid is c, the activity of hydrogen ion is $c\gamma$, and the free-energy increase attending the transfer of 2 mols of it from unit activity to an activity $c\gamma$ is given by equation (9),

$$\Delta \mathbf{F}_c = 2RT \ln c\gamma = RT \ln (c\gamma)^2.$$

Upon adding the equations for these three steps, equating to $-2E_1F$, the free-energy increase for the direct change, and solving for E_1, we have

$$E_1 = E^0_H - \frac{RT}{2F} \ln \frac{(c\gamma)^2}{p}. \qquad (10)$$

Since the energy quantity EF is expressed in joules, R should be in the same units, that is, $R = 8.316$.

Calculations of Other Electrode Potentials.—An expression similar to the one just given for a hydrogen electrode may be derived for the potential of any electrode in terms of its specific electrode potential. There should first be written down the electrode reaction, employing a suitable number of faradays of positive electricity on the left-hand side of the equation. Then the logarithmic term is written so that it contains in its numerator the activities of the substances formed by the electrode reaction and in its denominator the activities of the substances used in the reaction. When any of these substances are gases, it is customary to replace their activities by the partial pressures in atmospheres.

Let the general chemical reaction for any electrode be denoted by the production of c mols of the substance C and d mols of the substance D from a mols of substance A and b mols of B by the use of N faradays of positive electricity. The chemical equation for this change is written

$$aA + bB + \ldots + N \oplus = cC + dD + \ldots$$

Further, let E^0 be the electrode potential corresponding to unit activity (or pressure) of each substance involved; then E, the electrode potential corresponding to any other concentration of the reacting substances and reaction products, is

$$E = E^0 - \frac{RT}{NF} ln \frac{a_C^c a_D^d}{a_A^a a_B^b}. \tag{11}$$

where a_A, etc., represent the activities of the solutes. A few examples will serve to illustrate further the use of this general equation. At a chlorine electrode the reaction is

$$2Cl^-(C \text{ molal}) + 2 \oplus = Cl_2(p \text{ atm.})$$

and the electrode potential in terms of the normal chlorine electrode E^0_{Cl} is found by a process similar to that used on the hydrogen electrode, or from the general equation given above as

$$E = E^0_{Cl} - \frac{RT}{2F} ln \frac{p_{Cl_2}}{(C\gamma)^2}. \tag{12}$$

Similarly, at an electrode of iron dipping into ferrous sulfate, the electrode reaction is

$$Fe + 2\oplus = Fe^{++}(C \text{ molal})$$

and the electrode potential in terms of a specific electrode potential E^0_{Fe} corresponding to iron against hypothetical molal ferrous ion, or ferrous ion at unit activity, is

$$E = E^0 - \frac{RT}{2F} ln(a_{Fe^{++}}). \tag{13}$$

There is another kind of electrode reaction which causes no change in the number of mols of solute present, but only a change in the state of oxidation of the solutes. The ferrous-ferric electrode is an example; it consists of a platinum plate dipping into a solution containing ferrous ions and ferric ions. Its electrode reaction is

$$Fe^{++}(C_1) + \oplus = Fe^{+++}(C_2)$$

and the electrode potential corresponding to any concentrations of each ionic species, in terms of the potential when ferrous ions and ferric ions are each at unit activity, is

$$E = E^0 - \frac{RT}{F} ln \frac{(C_2\gamma_2)}{(C_1\gamma_1)}. \tag{14}$$

An electrode which functions as a chloride ion electrode consists of silver coated with silver chloride and dipping into a chloride solution. The electrochemical reaction is

$$Ag(\text{solid}) + Cl^-(C \text{ molal}) + \oplus = AgCl(\text{solid}),$$

and its electrode potential in a chloride ion solution of any concentration is

$$E = E^0 - \frac{RT}{F} ln \frac{1}{(C\gamma)}. \tag{15}$$

It should be noted that the concentrations of solid substances are not included in the logarithm term. Only those substances which are gases or solutes appear in the expression, just as in formulating mass-action expressions.

Normal Chlorine Electrode Potential.—Consider again the cell

$$H_2 \text{ (1 atm.)}, \text{ HCl (0.1 } m.\text{)}, Cl_2 \text{ (1 atm.)}; \quad E = 1.4881 \text{ } v.$$

The total electromotive force of this cell is the difference between two electrode potentials; the normal hydrogen electrode E^0_H has been defined as of zero potential. Then a value of E_1 for hydrogen gas against a solution which is 0.1 molal in hydrogen ions may be calculated from the activity coefficient of hydrogen ion in 0.1 $m.$ hydrochloric acid in the way explained above. A similar calculation of E_2 may be made in terms of the normal chlorine electrode potential E^0_{Cl} and the activity coefficient for chloride ions.

It is the difference $E_1 - E_2$ which is 1.4881 volts. If we assume that the activity coefficients for hydrogen ions and for chloride ions are the same in 0.1 $m.$ hydrochloric acid, this difference becomes

$$1.4881 = \left[E^0_H - \frac{RT}{2F} ln(0.1\gamma)^2\right] - \left[E^0_{Cl} - \frac{RT}{2F} ln \frac{1}{(0.1\gamma)^2}\right].$$

If γ is taken as 0.82 (from Fig. 49, page 210) and we solve this expression for E^0_{Cl}, we find

$$E^0_{Cl} = -1.4881 - \left[\frac{8.316 \times 298 \times 2.303}{2 \times 96{,}500} \log (0.082)^4\right]$$

$$= -1.360 \text{ volts at } 25°.$$

This is the potential of chlorine gas in contact with an inert metal dipping into a solution of chloride ions at unit activity. Such a normal electrode potential may be used to calculate an electrode potential of chlorine gas against solutions of chloride ions for which activity coefficients are known.

Normal Calomel Electrode.—A much more definite, and therefore much better, standard electrode is the normal calomel electrode

$$Hg \text{ (liq.)} + Hg_2Cl_2 \text{ (solid)}, KCl \text{ (1 molal)},$$

which is defined in terms of the total electrolyte, and is, therefore, a perfectly definite standard, reproducible in any laboratory without any assumption regarding activities. Many of the electrode potentials in the following table have been computed

from measurements against the normal calomel electrode by adding to these measured potentials that of the cell[1]
H_2(1 atm.), H^+ (unit activity)||KCl (1 molal), Hg_2Cl_2 + Hg, for which the electromotive force has been calculated as 0.2828 volt, by several investigators.[2] In the equations above given for calculating the electromotive force of simple cells, it does not matter whether electrode potentials referred to the one or other standard electrode are used, so long as both E^0 values employed in any calculation are referred to the same standard.

In the cell above whose electromotive force is 0.2828, E_1 is zero by the convention we have adopted, and E_2 is -0.2828. It will be observed that in Table 126 the potential of the electrode

$$Hg + Hg_2Cl_2, Cl^-$$

is -0.2700, and not -0.2828. The value -0.2828 is for KCl at unit *molality*, and in such a solution the activity of chloride ion is about 0.82, while -0.2700 applies to a solution of chloride ions at unit *activity*.

Electrolysis and Electrode Potential.—When the elements are arranged in the order of decreasing electrode potential, the order is the "electromotive series" mentioned in inorganic chemistry. In electrolysis, that ion which requires the lowest discharge potential will be deposited first. For example, in electrolysis of a solution of sodium chloride, using a cathode coated with silver chloride, the reaction

$$AgCl\ (solid) = Ag\ (solid) + Cl^- + \oplus$$

[1] There is a small potential resulting from the junction of two solutions of different solutes, or a junction of two concentrations of the same solute. This small potential has been subtracted from the total potential of the cell, a fact which is indicated in cells by inserting two vertical lines between the solutions as is done above. Correcting for junction potentials is a difficult task; the potentials involved are usually only a few thousandths of a volt, and junction potentials calculated by two different investigators do not quite agree. The calculation is described by Lewis and Sargent (*J. Am. Chem. Soc.*, **31,** 363 (1909)) for a junction between unlike solutes at the same concentration, and by MacInnes (*J. Am. Chem. Soc.*, **37,** 2301 (1915)) for a single solute at different concentrations on the two sides of a liquid junction.

[2] Lewis, Brighton, and Sebastian, *J. Am. Chem. Soc.*, **39,** 2245 (1917); MacInnes, *J. Am. Chem. Soc.*, **41,** 1086 (1919); Beattie (*J. Am. Chem. Soc.*, **42,** 1128 (1920)) finds 0.2826; Noyes and Ellis (*J. Am. Chem. Soc.*, **39,** 2543 (1917)) find 0.2824.

requires a potential of -0.2238 volt; that is, a potential which will cause this electrode reaction is still 0.2238 volt too low for the deposition of hydrogen. The potential required to deposit any ion at a cathode must be greater than its own electrode

TABLE 126.—NORMAL ELECTRODE POTENTIALS AT 25°

Electrode	E^0	Electrode	E^0
Li, Li^+ [1]	2.957_8	Ag, Ag^+ [6]	-0.799_5
Rb, Rb^+ [4]	2.924_2	Pt, I_2, I^-	-0.535_7
K, K^+ [3]	2.922_4	Pt, Br_2, Br^- [10]	-1.065_9
Na, Na^+ [2]	2.712_5	Pt, Cl_2, Cl^- [11]	-1.359_4
Zn, Zn^{++}	0.758_1	Pt, H_2, OH^-	$+0.828_0$
Fe, Fe^{++}	0.44_1	Ag + AgCl, Cl^- [7]	-0.2238
Cd, Cd^{++}	0.397_6	Hg + Hg_2Cl_2, Cl^- [7]	-0.2700
Tl, Tl^+	0.336_2	Cu, Cu^+	-0.510
Sn, Sn^{++} [5]	0.13_6	M, Fe^{+++} + Fe^{++} [8]	-0.739
Pb, Pb^{++} [5]	0.12_2	Hg + Hg_2Cl_2, KCl [8]	-0.2828
Pt, H_2, H^+ [8]	0.000_0	Cu + CuCl, Cl^- [9]	-0.12
Cu, Cu^{++}	-0.344_3	O_2 (1 atm.), OH^-	-0.393
Hg, Hg_2^{++}	-0.798_6	Ag + AgI, I^-	-0.15

The single potentials listed in this table are taken from GERKE, *Chem. Rev.*, **1**, 377 (1925), who has compiled them for the International Critical Tables. The numbers in parentheses in the table refer to original papers containing data on these electrode potentials, as follows:

[1] LEWIS and KRAUS, *J. Am. Chem. Soc.*, **35**, 341 (1913).
[2] LEWIS and KRAUS, *J. Am. Chem. Soc.*, **32**, 1459 (1910).
[3] LEWIS and KEYES, *J. Am. Chem. Soc.*, **34**, 119 (1912).
[4] LEWIS and ARGO, *J. Am. Chem. Soc.*, **37**, 1989 (1915).
[5] GETMAN, *J. Am. Chem. Soc.*, **40**, 619 (1918).
[6] NOYES and BRANN, *J. Am. Chem. Soc.*, **34**, 1016 (1912).
[7] NOYES and ELLIS, *J. Am. Chem. Soc.*, **39**, 2541 (1917).
[8] LEWIS, BRIGHTON, and SEBASTIAN, *J. Am. Chem. Soc.*, **39**, 2258 (1917).
[9] NOYES and CHOW, *J. Am. Chem. Soc.*, **40**, 739 (1918).
[10] LEWIS and STORCH, *J. Am. Chem. Soc.*, **39**, 1910 (1917).
[11] LEWIS and RUPERT, *J. Am. Chem. Soc.*, **33**, 299 (1911).

potential or it would pass back into solution when present, therefore would not deposit from a solution at all. But the tendency of sodium ions to be deposited at this electrode is small, for the electrode potential of sodium is very high. The potential which would cause hydrogen to deposit is 2.715 volts below that

required to deposit sodium. During this electrolysis, silver chloride will be reduced to silver until all of it is exhausted; then hydrogen ions will discharge and leave hydroxyl ions behind, but sodium will not deposit at all under the conditions of electrolysis.

It will be seen from this statement that the electrode potential of sodium has not been determined by a single step. It was, in fact, determined in two steps, the first of which measured the potential of sodium against a dilute sodium amalgam through a solution in a non-aqueous solvent; the second step determined was the potential of this amalgam against the hydrogen electrode in sodium hydroxide solution.

Electromotive Force and Ion Activity.—We have already seen that a normal electrode potential can be calculated from the electromotive force of a cell involving a dilute solution. Conversely, from the measured electromotive force in a cell with some other concentration of solution, we can calculate the ion activity. The electromotive force of the cell H_2 (1 atm.), HCl (C molal), Cl_2 (1 atm.) is $E_1 - E_2$, and each of these values may be computed from the normal or specific electrode potentials in Table 126 by means of equations (10) and (12) above, each of which equations is a special case of equation (11). But the ion *activities* so computed differ from the ion *concentrations* based on mol numbers obtained from freezing-point determinations, or from the ratio of equivalent conductances, and the differences are considerable. Thus in computing the activity coefficient of tenth normal hydrochloric acid from that of thousandth normal acid, 0.82 is obtained by the electromotive force method, and 0.92 is conductance ratio. It is the fraction 0.82 which is commonly called the activity coefficient in tenth normal hydrochloric acid, where the activity or effective concentration of hydrogen ion is 0.082. As has been mentioned on page 210, accurate freezing-point data may be used to calculate activity coefficients, but the mol number may not be taken as $1 \pm \gamma$, as was formerly supposed.

One of the serious problems in connection with the ionic theory is the lack of an adequate explanation of this difference. For very dilute solutions the activity ratios and conductivity ratios are in substantial agreement; in strong solution there is a wide difference which is not due to experimental errors. In

fact, it is this serious difference which has led some chemists to discard the idea of fractional ionization, to assume complete ionization, and to seek some other explanation for change of activity ratio and of conductivity ratio with changing concentration.

Concentration Cells.—When two separate cells which differ only in the concentration of electrolyte in them are connected in opposition, and positive electricity is passed through the whole combination, the net effect is the transfer of solute from one concentration to another. As an example, consider the cells

$$\text{AgCl} + \text{Ag, HCl } (C_1), \text{ H}_2 \frown \text{H}_2, \text{ HCl } (C_2), \text{ AgCl} + \text{Ag.}$$

When a faraday of electricity is passed through the whole system considered as a single cell, the electrode reactions are

$$\text{Ag} + \oplus + \text{Cl}^- = \text{AgCl and } \text{H}^+ = \tfrac{1}{2}\text{H}_2 + \oplus$$

in the first cell, and

$$\tfrac{1}{2}\text{H}_2 + \oplus = \text{H}^+ \text{ and } \text{AgCl} = \text{Ag} + \oplus + \text{Cl}^-$$

in the second cell. The net effect of these two cells is, therefore, the formation of a mol of hydrogen chloride in the second cell and the loss of it in the first cell. For dilute acid solutions the electromotive force of the whole combination, considered as a single concentration cell, is shown by the equation

$$E = \frac{nRT}{F} ln \frac{C_1\gamma_1}{C_2\gamma_2}, \tag{16}$$

where n is the number of mols of ion solute transferred from the ion activity $C_1\gamma_1$ to the activity $C_2\gamma_2$ per faraday of electricity. The derivation of this equation follows very simply from equation (9) for the transfer of a solute from one activity to another. For each mol transferred the free-energy increase is

$$\Delta\mathbf{F} = RT\, ln \frac{a_2}{a_1}.$$

and on passing 1 faraday through the two cells one mol of hydrogen ion and one of chloride ion are transferred from activity $C_2\gamma_2$ to $C_1\gamma_1$. The free-energy increase is also given by $-EF$, and on solving the equality

$$-EF = 2RT\, ln \frac{C_2\gamma_2}{C_1\gamma_1}$$

for E, the electromotive force of the whole concentration cell, equation (16) results.

Such calculations of ion activity in one solution from that in another solution of the same solute at a different concentration may be based on electromotive force measurements of single cells of the type

$$H_2 \text{ (1 atm.), HCl } (C), \text{ AgCl (solid)} + \text{Ag.}$$

Measurements for this cell at several temperatures[1] and for various concentrations of hydrochloric acid are given in Table 127.

TABLE 127.—ELECTROMOTIVE FORCE OF THE CELL H_2, HCl, AgCl + Ag

Mols HCl per 1000 grams water	Electromotive force at		
	15°	25°	35°
0.33314	0.29678	0.29348	0.28958
0.10000	0.35375	0.35221	0.35031
0.09534	0.35600	0.35453	0.35270
0.03324	0.40530	0.40545	0.40513
0.00948	0.46452	0.46666	0.46824
0.003378	0.51325	0.51696	0.52023

If the first two of these cells are connected in opposition at 25°, the net electromotive force is the difference between those of the separate cells, and the change in state of the system as a whole is a transfer of hydrochloric acid from one solution to the other. If the transfer takes place from the stronger into the more dilute solution, the electromotive force is 0.05873 volt. Assuming the activity coefficient in 0.1 formal hydrochloric acid to be 0.82 (from Table 75), the activity of each ion in the stronger solution may be computed from equation (16). Two mols of solute are transferred per faraday of electricity, a mol of hydrogen ion and a mol of chloride ion. Then

$$0.0587 = \frac{2 \times 8.316 \times 298 \times 2.303}{96{,}500} \log \frac{a_2}{0.082};$$

[1] NOYES and ELLIS, *J. Am. Chem. Soc.*, **39**, 3532 (1917).

whence $\log \frac{a_2}{0.082}$ is 0.496, and a_2 is 0.257 in a solution in which the acid concentration is 0.333. The activity coefficient, is, therefore, 0.257/0.333 = 0.78. In the same way, the activity coefficient in solutions of other concentrations may be calculated from equation (16) by taking the difference between the electromotive force of the 0.1 molal cell and that involving any other concentration of acid. When this is done, activity coefficients in substantial agreement with those of Table 77 on page 211 are obtained. Many investigators have attempted with more or less success to extrapolate a plot of some function of the activity against the concentration into the region of such great dilution that the activity coefficient becomes unity. The various methods of doing this lead to slightly different relative values for activity coefficients, such as those for potassium chloride in Table 76. In place of entering into a discussion of these methods, we shall consider the procedure outlined in the previous paragraph as yielding activity coefficients of sufficient accuracy for our purpose.[1] Other methods of obtaining them are suggested on page 209.

Amalgam Concentration Cells.—Differences between ion activities and molal concentrations are not confined to aqueous solutions of ionized salts; a similar effect is observed in concentration cells consisting of amalgams of thallium (and other metals) in mercury. For example, a cell at 15° composed of two amalgams containing different amounts of thallium and in contact with a solution of thallous chloride,

$$\text{Hg} + \text{Tl (0.410 per cent)}, \text{TlCl}, \text{Hg} + \text{Tl (0.111 per cent)},$$

operates by transferring thallium from one amalgam to the other. At the left-hand side the reaction is $\text{Tl} + \oplus = \text{Tl}^+$, and at the right it is $\text{Tl}^+ = \text{Tl} + \oplus$. The change of state per faraday is the transfer of an atomic weight of thallium from one amalgam to the other, and the potential of the cell is independent of

[1] For an excellent exposition of the various methods for calculating activity coefficients, see pages 326 to 385 of LEWIS and RANDALL'S "Thermodynamics," McGraw-Hill Book Co., Inc.

the electrolyte concentration. Applying equation (16) to calculate the electromotive force of this cell, we find

$$E = \frac{8.32 \times 288 \times 2.303}{96{,}500} \log \frac{0.410}{0.111} = 0.0340,$$

while actual experiment[1] gives 0.0348; the difference is 2.5 per cent of the measured value, and it shows that the activity of thallium dissolved in mercury is not proportional to its weight concentration. Similar experiments with indium amalgams lead to somewhat better agreement between observed and calculated potentials, but the potential between tin amalgams containing respectively 0.66 and 0.20 per cent of tin by weight is only 85 per cent of that calculated from the ideal equation. In all of the amalgam cells, results approaching those derived from equation (16) were obtained as the amalgams employed were made more and more dilute.[2]

Electromotive Force and Chemical Equilibrium.—We shall now consider several examples of the use of normal electrode potentials in determining conditions of chemical equilibrium. It has already been stated that the driving force of a cell is the driving force of the chemical reaction taking place in it. When, therefore, equilibrium is reached, there is no tendency for the chemical reaction to proceed one way or the other, and there is no electromotive force. We need not set up a cell in which there is no electromotive force developed, however, in order to determine equilibrium conditions. Let us consider the cell

$$\text{Ag} + \text{AgCl, HCl (0.1 formal), } \text{Cl}_2 \text{ (1 atm.)}; \; E = 1.142 \; v.$$

The hydrochloric acid in this cell is saturated with silver chloride, which gives rise to a very small concentration of silver ions such that the solubility product $(\text{Ag}^+)(\text{Cl}^-)$ is satisfied, and, on account of the very small concentration involved, this product is practically S_0^2, where S_0 is its solubility in pure water. The chloride ion activity in 0.1 formal hydrochloric acid is about 0.082; the silver ion activity may be computed from the electromotive force. This cell may also be written

$$\text{Ag, Ag}^+ \; (a) + \text{Cl}^- \; (0.082), \; \text{Cl}_2 \text{ (1 atm.)}; \; E = 1.142 \; v.,$$

[1] Richards and Wilson, *Carnegie Inst. Publ.*, **118**, 22 (1909).

[2] See also Richards and Daniels, *J. Am. Chem. Soc.*, **41**, 1732 (1919).

where a denotes the silver ion activity in a solution 0.1 formal in hydrochloric acid and saturated with silver chloride. At the left-hand electrode the reaction is $Ag + \oplus = Ag^+$, and

$$E_1 = E^0_{Ag} - \frac{RT}{F} ln\ a.$$

At the right-hand electrode the chemical reaction is

$$2Cl^- + 2\oplus = Cl_2\ (1\ atm.),$$

and the electrode potential is

$$E_2 = E^0_{Cl} - \frac{RT}{2F} ln \frac{1}{(0.082)}.$$

The difference $E_1 - E_2$ is the electromotive force of the cell. Substituting the above expressions, we have

$$1.142 = E^0_{Ag} - \frac{RT}{F} ln\ a - \left[E^0_{Cl} + \frac{RT}{2F} ln\ (0.082)^2\right]$$

$1.142 = -0.799 - 0.0592 \log a - (-1.362) - 0.0592(-1.076)$ or, upon solving for $\log a$,
$\log a = -8.70$; whence $a = 0.2 \times 10^{-8} = (Ag^+)$ in 0.1 formal HCl. The chloride ion activity in 0.1 formal hydrochloric acid is 0.082, and the solubility product for silver chloride is $0.082 \times 0.2 \times 10^{-8} = 1.64 \times 10^{-10}$; the square root of this figure is 1.3×10^{-5}, which is the value for the solubility of silver chloride in pure water based on this calculation. Other experiments yield solubilities of 1.1 to 1.2×10^{-5}.

As another example of the application of electromotive force to chemical equilibrium, consider the reaction

$$Sn\ (solid) + Pb(ClO_4)_2 = Pb\ (solid) + Sn(ClO_4)_2,$$

for which data have been given on page 300, showing that at equilibrium the ratio $(Sn^{++})/(Pb^{++}) = 2.98$ from a purely chemical method of experiment. At equilibrium the electromotive force of the cell

$$Sn,\ Sn(ClO_4)_2\ (C_1) + Pb(ClO_4)_2\ (C_2),\ Pb$$

will be zero, whence E_1 is equal to E_2. We shall compute the two electrode potentials, equate them, and solve for the ratio

$(Sn^{++})/(Pb^{++})$, following the method already used on other electrodes. The electrode potential of the tin electrode is

$$E_1 = E^0_{Sn} - \frac{RT}{2F} ln\ (C_1\gamma_1),$$

corresponding to the chemical equation $Sn + 2 \oplus = Sn^{++}$; and at the lead electrode the chemical reaction written in the usual way is $Pb + 2 \oplus = Pb^{++}$, for which the electrode potential is

$$E_2 = E^0_{Pb} - \frac{RT}{2F} ln\ (C_2\gamma_2).$$

Equating these two electrode potentials, assuming the two activity coefficients to be equal, and solving for the ratio of tin to lead in solution, we have

$$E^0_{Sn} - E^0_{Pb} = \frac{RT}{2F} ln \frac{(Sn^{++})}{(Pb^{++})},$$

whence

$$\log \frac{(Sn^{++})}{(Pb^{++})} = \frac{0.136 - 0.122}{0.0296} = 0.473; \text{ and } \frac{(Sn^{++})}{(Pb^{++})} = 2.97.$$

This illustrates a method of obtaining equilibrium data from specific electrode potentials, or a method of calculating one electrode potential from another by means of equilibrium measurements.[1]

Ionization Constant of Water.—From measurements of cells of the type

$$H_2,\ KOH,\ KCl,\ HCl,\ H_2$$

there is obtained, after correction for the liquid potentials between the alkali and salt solution, and between the salt solution and acid, an electromotive force which is equivalent to that of a cell[2]

$$H_2\ (1\ atm.),\ OH^- \| H^+,\ H_2\ (1\ atm.);$$

and with hydrogen ion at unit activity on the right-hand side and hydroxide ion at unit activity on the left-hand side the measured electromotive force at 25° is 0.8278 volt. The ionization constant

[1] Noyes and Toabe, *J. Am. Chem. Soc.*, **39**, 1537 (1917).

[2] Lewis, Brighton, and Sebastian, *J. Am. Chem. Soc.*, **39**, 2245 (1917).

of water is the product of the ion concentrations of hydrogen and hydroxide ions in any solution. In the left-hand solution hydrogen ions exist in exceedingly small concentration, but their activity may be calculated from the electrode potential, since this cell may be considered as equivalent to

$$H_2 \text{ (1 atm.)}, H^+ \text{ (at } C) \| H^+ \text{ (unit activity)}, H_2 \text{ (1 atm.)},$$

for which E_2 is zero, and hence E_1 is the measured electromotive force of the cell. Then

$$E_1 = 0.8278 = E^0_H - \frac{RT}{F} ln\, C = 0 - 0.0592 \log C$$

$$\log C = -\frac{0.8278}{0.0592} = -14.0.$$

Then the concentration of hydrogen ion is 10^{-14}, and this is the value of $K_w = (H^+)(OH^-)$ sought.[1]

Titration in Colored or Turbid Solutions.—It is sometimes desired to titrate to neutrality a solution which is so cloudy that ordinary color indicators are useless. This may be accomplished readily by means of electromotive force measurements, since near the end point of a titration the hydrogen ion concentration changes rapidly. Suppose a platinum plate to dip into the solution to be titrated, hydrogen to bubble over the plate, and connection to be established with a normal calomel electrode through a very small tube so that none of the unknown solution is lost. Table 128 below shows the concentration of hydrogen ion at several stages of a titration, supposing 100 c.c. of 0.20 normal acid to be titrated with 0.20 normal alkali. For example, when 99 c.c. of alkali have been added, assuming a strong acid to be present, only 1 per cent of the acid remains untitrated, the total volume of solution has increased to 199 c.c., and it contains 0.0002 formula weight of acid, hence the acid concentration is now approximately 0.001 normal. When 99.9 c.c. of alkali have been added, the acid concentration is 0.0001 normal; when 100 c.c. have been added, the hydrogen ion concentration is that of pure water, and for 100.1 c.c. of alkali the solution is made 0.0001

[1] Similar results are obtained by Lorenz and Bohi (*Z. physik. Chem.*, **66**, 733 (1909)) from a cell H_2, HCl (0.1*f.*)‖KOH (0.1 *f.*), H_2; E = 0.6980 at 25°. Assuming the activity coefficient in each solution to be 0.82, log K_w is −13.9 and K_w is 1.2×10^{-14}.

TABLE 128.—HYDROGEN ION CONCENTRATION IN A SOLUTION OF ACID DURING TITRATION WITH ALKALI

Volume of 0.2 normal base added to 100 c.c. of 0.2 normal acid	Hydrogen ion concentration if the acid is		Electromotive force for	
	Hydrochloric acid	Acetic acid	Hydrochloric acid	Acetic acid
98.0	1.9×10^{-3}	2×10^{-7}	0.443	0.679
99.0	9.5×10^{-4}	10^{-7}	0.462	0.707
99.5	4.7×10^{-4}	5×10^{-8}	0.477	0.715
99.8	2×10^{-4}	2×10^{-8}	0.561	0.739
100.0	10^{-7}	10^{-9}	0.697	0.816
100.2	5×10^{-11}	5×10^{-11}	0.893	0.893
100.5	2×10^{-11}	2×10^{-11}	0.917	0.917
101.0	10^{-11}	10^{-11}	0.934	0.934
102.0	5×10^{-12}	5×10^{-12}	0.952	0.952

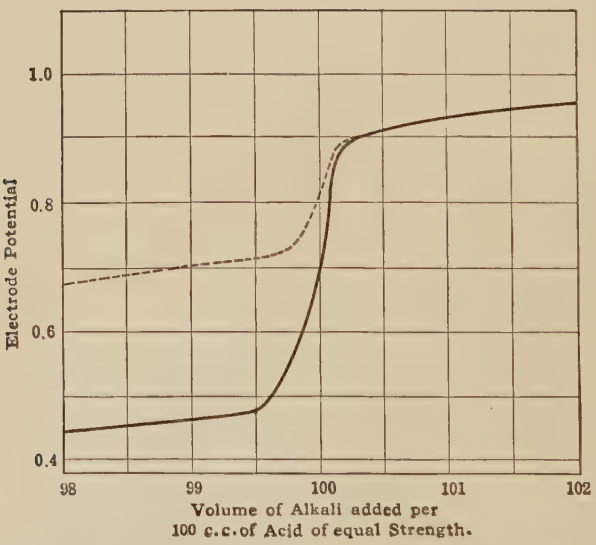


FIG. 81.—Showing change of electromotive force with progress of titration. The cell consists of a hydrogen electrode dipping into an acid solution, and connected to a normal calomel electrode. (Hydrochloric acid is shown by a solid line, acetic acid by the dotted line.)

normal in hydroxide ions, or $10^{-14}/0.0001 = 10^{-10}$ in hydrogen ions. Thus the last two drops change the logarithm of the hydrogen ion concentration from -4 to -7, and the first drops in excess change it from -7 to -10. Each of these changes corresponds to a change of nearly 0.18 volt in the electromotive force of the cell of which the unknown solution forms a part. Therefore a plot of observed electromotive force against the number of cubic centimeters of alkali added would show a sharp rise at the end point.

This is illustrated in Fig. 81 above, for a strong acid, and for acetic acid, whose salt is hydrolyzed in dilute solution. It will be noted that in both cases there is a sharp break in the curve of measured electromotive force plotted against volume of base added, which indicates clearly the end point of the titration. Such a process is especially useful in connection with biological experiments. Similar curves showing complete oxidation of a ferrous salt to ferric salt may be obtained by plotting the buret readings against measured potential. Such electrometric titrations are beginning to receive the attention they deserve from analytical chemists. As the change in potential at the end point is relatively large, no sensitive galvanometer is required, and relatively simple apparatus for such experiments may now be obtained.

Concentration Cells with Transference.—There is another type of concentration cell whose change in state corresponds only to the transfer of a solute from one concentration to another, but which involves only a single set of electrodes. As an example we may consider the cell

$$H_2,\ HCl\ (C_2),\ HCl\ (C_1),\ H_2,$$

and pass 1 faraday of positive electricity through it. The electrode reactions are $\frac{1}{2}H_2 + \oplus = H^+$ at the left and $H^+ = \frac{1}{2}H_2 + \oplus$ at the right, hence by electrolysis there has been formed at the left one mol of hydrogen ion into a concentration C_2, and there has been removed from solution at C_1 one equivalent of hydrogen ion. Electricity is carried *through* the solutions by hydrogen ions and chloride ions in quantity proportional to their respective ionic velocities. That is, denoting by T_{Cl} the transference number of chloride ions, for each faraday of elec-

tricity carried through the cell T_{Cl} faradays will be carried by T_{Cl} equivalents of chloride ion moving from right to left, and $(1 - T_{Cl})$ faradays will be carried by hydrogen ions moving from left to right. Then the left-hand portion of the cell will gain by transference T_{Cl} equivalents of chloride ion and lose by transference $(1 - T_{Cl})$ equivalents of hydrogen ion. Its net effect per faraday is the gain of T_{Cl} equivalents of both hydrogen ion and chloride ion. At the right-hand electrode T_{Cl} equivalents of chloride ions are lost by transference, and $(1 - T_{Cl})$ equivalents of hydrogen ion are gained by transference. Hence the net effect is the loss of T_{Cl} equivalents of hydrogen ion and of chloride ion when the effects of both electrolysis and transference are considered. Considering now the cell as a whole, each faraday of electricity results in transferring T_{Cl} equivalents of hydrochloric acid from the right-hand side of the cell to the left-hand side. Applying the formula given above for concentration cells, and considering hydrogen ion and chloride ion as each constituting a mol of solute, we have $n = 2T_{Cl}$, and

$$E = \frac{2T_{Cl}RT}{F} ln \frac{C_1\gamma_1}{C_2\gamma_2}. \qquad (17)$$

From electromotive force measurements of cells of this type (called cells with transference) and of the type first given (called cells without transference) it is possible to determine the transference number, since it will be seen upon dividing equation (17) by equation (16) that the ratio of the electromotive forces is the transference number direct.[1]

Electromotive Force and Heat of Reaction.—Chemical reactions which proceed vigorously evolve large quantities of heat in many cases. When these same reactions are caused to take place in electric cells or batteries, electrical energy is given out in place of heat. Naturally, a given quantity of energy cannot appear as heat and still be used to generate electricity. In many cells the quantity of electric energy is roughly equal to the heat of the reaction when carried out in a calorimeter,

[1] Examples of such measurements are given by MacInnes and Parker (*J. Am. Chem. Soc.*, **37**, 1445 (1915)) for potassium chloride, and by MacInnes and Beattie (*J. Am. Chem. Soc.*, **42**, 1117 (1920)) for lithium chloride. These papers will be difficult reading for beginners, but are very profitable reading for anyone really interested in the method.

and it was at first thought that the electromotive force of a cell could be computed from the heat effect simply by equating $-EnF$ to ΔH the heat of reaction. In order to test this belief, it is only necessary to place an electric cell in a calorimeter and let it operate. If any heat is absorbed by the calorimeter during the electric operation of the cell, the simple equivalence of ΔH and $-ENF$ is not to be expected. If during its operation the cell absorbs heat from the calorimeter, the electric energy output will be greater than the heat of reaction by the quantity of heat absorbed from the calorimeter and changed into electric energy. Usually there is not a very large evolution or absorption of heat during the operation of an electric battery, and the relation $-ENF = \Delta H$ is *roughly* satisfied in many batteries.

A strict relation between electromotive force and heat of reaction is that known as the Gibbs-Helmholtz equation,

$$\frac{ENF + \Delta H}{T} = NF\frac{dE}{dT}, \tag{18}$$

where dE/dT is the rate of increase of electromotive force with increasing temperature. It will be seen from the equation that when dE/dT is zero, that is, when the electromotive force does not change with temperature, the heat absorbed by the reaction is equal to the electric energy $-ENF$. In other words, the approximation that the heat evolved by a reaction is equal to the electric energy derivable from it is more nearly true the smaller the temperature coefficient of electromotive force. In using the Gibbs-Helmholtz equation the heat absorbed by the reaction must be expressed in joules since the term ENF appearing beside it is in joules. A calorie is 4.182 joules.

The integral of this equation between two temperature limits over which the heat of reaction is substantially constant is

$$\frac{E_2}{T_2} - \frac{E_1}{T_1} = \frac{-\Delta H}{NF}\left(\frac{1}{T_2} - \frac{1}{T_1}\right). \tag{19}$$

Let us illustrate the application of this equation by means of the second cell of Table 127, using E_2 as the electromotive force at 35°, where T is 308°. The chemical reaction corresponding to 2 faradays passing through the cell is

$$H_2 \text{ (1 atm.)} + 2AgCl \text{ (solid)} = 2HCl \text{ (in 0.1 } m.\text{)} + 2Ag \text{ (solid)}$$

and upon substituting in equation (19), it is a value for this heat of reaction which is obtained:

$$\frac{0.35031}{308} - \frac{0.35375}{288} = \frac{-\Delta H}{2 \times 96{,}500}\left(\frac{1}{308} - \frac{1}{288}\right),$$

whence ΔH is $-77{,}870$ joules or $-18{,}900$ cal.

The heat of dilution of hydrochloric acid may also be calculated from Table 127 by means of equation (19). Since, when two cells are connected in opposition, the net effect of the pair is the transfer of hydrogen chloride from one concentration to another, the electromotive force at 15° of such a pair is 0.05697 if the first two cells of Table 127 are used to transfer hydrochloric acid from 0.33314 to 0.1000 formal; the corresponding electromotive force at 35° is 0.06073 volt. Substitution in equation (19) leads to a value of the heat of dilution as follows:

$$2HCl \text{ (at } 0.333\ m.) = 2HCl \text{ (at } 0.10\ m.);\ \Delta H = -520 \text{ joules.}$$

Questions

1. The electromotive force of a certain cell is higher at 25 than at 0°C. Does it evolve heat during its electric operation or absorb heat?

2. Calculate from the normal electrode potentials the electromotive force of the cell $Hg + Hg_2Cl_2$, HCl (0.1m.), Cl_2 (1 atm.). The experimentally determined value is 1.0896 volts.

3. When one mol of hydrogen chloride is formed from its elements, 22,000 cal. are evolved, and when this is dissolved in 10 liters of water, 17,200 cal. are evolved. From these data and the electromotive force of the cell H_2, HCl (0.1f.), Cl_2(E = 1.4881), at 25°, calculate the electromotive force of this cell at 0°C.

4. Calculate the electromotive force of the cell H_2, (1 atm.), HCl (0.001f.), Cl_2 (1 atm.) at 25°, assuming 0.98 for the activity coefficient.

5. Calculate the "activity" or effective concentration of hydrogen ions and of chloride ions in 0.10 formal HCl from the measured electromotive force given in the text, and the normal electrode potentials.

6. The electrode potential of zinc is 0.76 volt; that of cadmium is about 0.42 volt. Calculate the equilibrium constant for the chemical reaction $ZnSO_4 + Cd = CdSO_4 + Zn$ at 25°.

7. Compute the electromotive force of the combination at 25°:

H_2, HCl (0.1n), HgCl + Hg ⌒ Hg + HgCl, HCl (0.001n), H_2. Use the data of Table 77 for the activity of hydrochloric acid. (Tolman and Ferguson, *J. Am. Chem. Soc.*, **34**, 232 (1912).)

8. Calculate the electromotive force of the cell Zn, $ZnSO_4$ (C_1), $ZnSO_4$ (C_2), Zn, at 25° when the first solution is 0.10 formal in zinc ion and the second is 0.0001 formal in zinc ion.

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